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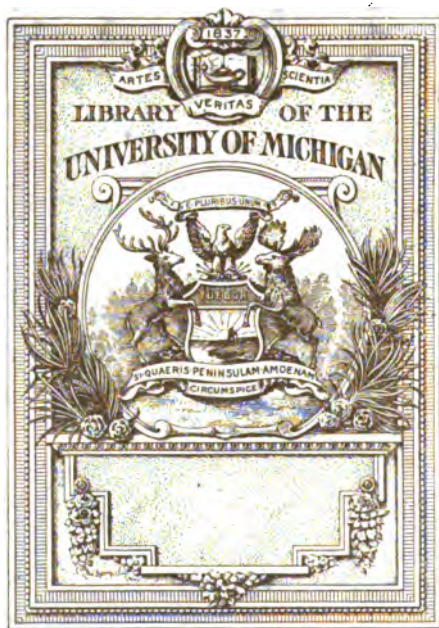
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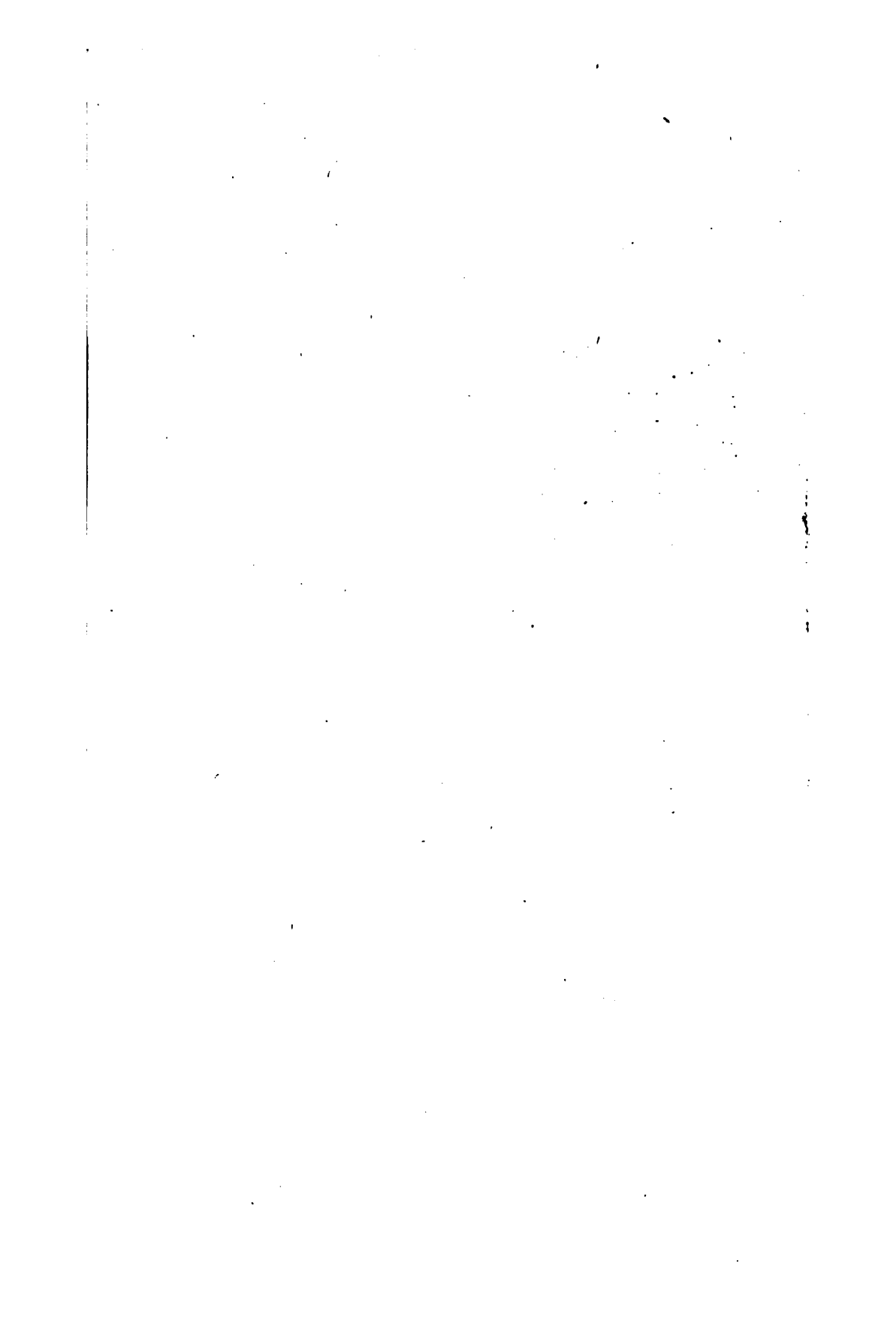
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A TREATISE
ON THE
DISTILLATION OF COAL-TAR
AND
AMMONIACAL LIQUOR,
AND THE
SEPARATION FROM THEM OF VALUABLE PRODUCTS.

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PREFACE.

THE distillation of coal-tar and the manufacture of ammoniacal compounds, which, for obvious reasons, is intimately connected with the former, have not previously been subjected to monographic treatment in the English language, although that industry is one of the most important branches among English chemical manufactures. Even in foreign languages, well-nigh the only special treatise on this subject is one published in the German language by the author in 1867. That treatise was principally founded on the author's own practical experience, and was very favourably received in Germany; but it is necessarily antiquated to some extent now, and many inquiries for a new edition have been made from time to time. This induced the author, in 1880, after he had completed his Treatise on Sulphuric Acid and Alkali, to take up coal-tar and ammonia again, and to renew his former practical acquaintance with their manufacture by personal observations in a series of the largest and best tar- and ammonia-works in England, France, and Germany, to the owners and managers of which he here begs to tender his best thanks.

In elaborating his notes into a new monograph, he has met with invaluable assistance from Mr. Watson Smith and Dr. C. Meymott Tidy. The former gentleman had the great kindness to write out his notes on coal-tar and ammonia for the special

benefit of the author; and his contributions (always marked as such) will be found in many parts of this book. He has, moreover, rendered great assistance in looking over the proof-sheets; but a few of his corrections were too late for the press, and will be found at the end of the book as "Errata."

It is hardly necessary to say that the literature of this branch of industry has been thoroughly studied, and that every thing the author deemed of sufficient importance will be found in this book. In the case of coal-tar he hopes to have attained to something like an exhaustive treatment; but in the case of ammonia an attempt at such a thing would have produced a bulky volume, containing endless repetitions and very much chaff interspersed with the wheat. The greatest stress has therefore been laid upon what is done in practice, and upon presenting a true picture of the actual state of this industry. A selection has been made of some of the more modern styles of apparatus and processes, which may be considered as fully representing every *essential* modification of manufacturing-practice; and these have been described in sufficient detail wherever possible.

The aim of the second and eleventh Chapters was not an exhaustive scientific treatment, but only a description of the more important properties of the components of coal-tar and gas-liquor, accompanied by quotations which will facilitate further studies thereon.

The author will be amply rewarded for his labour if it is found that this book has some useful knowledge to impart, and that it is to some little extent calculated to advance an important industry.

The Polytechnicum, Zurich,
May 1882.

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COAL-TAR AND AMMONIA.

CHAPTER I.

THE ORIGIN OF COAL-TAR.

THE process of destructive distillation of organic substances (that is, of heating them beyond the point of decomposition without access of air) is carried on for several industrial purposes. The principal object in view may be either the dry residue, or the gases evolved, or else the condensed distillate. The latter nearly always separates into two distinct layers, one of which consists of the water preexisting in the original substance, or formed from it during destructive distillation, holding in solution a portion of the distillate; the other layer is formed by the condensed products insoluble in water, appearing in the form of a more or less viscid dark-coloured oil, in some cases lighter, in others heavier than the watery distillate, and generally known by the name of *tar*.

According to the difference of the original materials, the products of their destructive distillation differ; but the difference is much greater in the condensed distillates than in either the solid residue or the permanent gases. The *solid residue* is always essentially carbon; at least it is usually assumed to be so. Hence the different qualities of wood-charcoal, coke, bone-charcoal, &c. would be principally caused by the various descriptions and quantities of mineral matter intimately mixed with the carbon remaining behind as the residuum of the organic matter, and varying according to the original substance. Along with this it should not be overlooked that the process of destructive distillation is industrially carried on at

very different temperatures, by which the physical nature of the carbonaceous residue is greatly modified. Probably this plays at least as important a part as the difference between the original materials. But it is also very possible that the molecules of carbon in wood-charcoal, coke, &c. do not consist of the same number of atoms. Lastly, it is certain that in these bodies, besides free carbon, certain compounds of carbon, hydrogen, and oxygen occur, the isolation or even the recognition of which has not yet been accomplished. In any case it cannot be denied that the *organic* portion of all carbonaceous residues, so far as the chemical reactions throw light upon it, does not present any great diversity.

The same can be said of the *permanent gases*, not remaining dissolved in the products of condensation, which are formed in destructive distillation. Carbon dioxide, carbon monoxide, nitrogen, hydrogen, the lowest members of the paraffin series, and of the hydrocarbons containing less hydrogen (ethylene, acetylene) are always found. Sulphuretted hydrogen does not occur in the distillation of wood, but occurs regularly in that of coal and of animal matters. The production of these permanent gases for illuminating-purposes is the object of a comparatively recent, but enormously important industry, in which now more than ever *coal* predominates almost to the exclusion of all other raw materials, except for very special purposes.

On the other hand, the *watery distillates* differ very much, according to the nature of the raw material. In the case of wood, which contains very little nitrogen, those products are of an acid nature, acetic acid being predominant, next to which methylic alcohol and acetone are the most important. The products originating from fossil vegetable substances behave in this respect similarly to wood, if they have been formed in the present or the more recent geological periods—for instance, peat and browncoal (lignite). The acid reaction of the distillate is frequently quoted as a criterion to distinguish browncoal from real coal. All the methylic alcohol and most of the acetic acid of commerce are obtained from this source. Real coal, on the other hand, which always contains a certain amount of nitrogen, always furnishes a watery distillate whose reaction is strongly alkaline, owing to the presence of ammonia and, to some extent, of volatile organic bases. The bulk of ammonia and ammonia-salts comes from this source, viz. the ammoniacal liquor of gas-works, which is obtained not merely by

simple air-condensation, but also by direct washing of the gas in the scrubbers.

A similar difference exists in the oily distillates, the *tars*. We may say, generally, that the tar from peat, browncoal, and bituminous shale consists *principally* of hydrocarbons of the "fatty" series; wood-tar, of phenols and their derivatives; coal-tar, of "aromatic" hydrocarbons. But along with the principal constituents there is always a large number of other compounds present; and matters are still further complicated by the fact that through the action of heat the individual compounds are transformed partly into other compounds of the same series, partly into compounds belonging to other series. Owing to this, tar obtained from the same material differs very much in composition according to the temperature of the dry distillation—nay, even according to the shape of the retorts, which allows more or less time of contact of the vapours with the hot sides of the vessel.

This explains why the tars are extremely complex mixtures, whose unravelling has not been any thing like completely accomplished even in the best-known case, that of coal-tar, much less in the other cases, owing to the extreme difficulties connected with this kind of research. It is true that acids (phenols) and alkalies can be separated at least by "serial reactions;" but the great bulk of indifferent hydrocarbons can only be separated from one another by fractional distillation, only a few of them by crystallization. Of these operations the first is often insufficient for isolating the simple compounds, especially those of high boiling-points, since at the boiling-temperature the compounds are frequently decomposed.

Browncoal-tar, as well as that obtained from peat and bituminous shale (and formerly also from the Torbane-Hill mineral), is manufactured for its own sake as a principal product, and forms the basis of the West-European manufacture of mineral oils and paraffin, which has proved its vitality even against the enormous competition of American and Russian petroleum, of ozokerite, and of other products ready formed in nature. The other products of the destructive distillation of such more recent fossils possess very little or no value, except in the case of some very dense, coal-like browncoals, which furnish good coke and good gas, but no mineral oil. On the contrary, *coal-tar* has up to the present nowhere been manufactured as a principal product, the other products playing an inferior part; it is only an accidental but unavoidable

by-product of the manufacture of lighting-gas from coals, exactly like the ammoniacal gas-liquor. It is imperative to condense these two substances in order to purify the gas; but whilst the coke remaining behind in gas-making was always a by-product of considerable value, which essentially influenced the cost price of the gas, tar and ammoniacal liquor were for many years regarded as refuse products which were not merely without value, but caused considerable inconvenience and expense for their removal. But since in the last quarter of a century coal-tar and ammoniacal liquor have become starting-points for a chemical industry of enormous dimensions, it can hardly be denied that circumstances might occur in which those two substances would be the principal products of the dry distillation of coal, so that the gas would only appear as a secondary product. Processes aiming at this have indeed been patented by Barrow (in 1862) and others. Thenius* proposes distilling coal in a special manner for tar, best of all by means of superheated steam. It is of historical interest that the first English patent referring to the destructive distillation of coal (that of John Joachun Becker and Henry Serle, dated August 19, 1681) does not treat of the manufacture of lighting-gas, but of "a new way of makeing pitch, and tarre out of pit coale, never before found out or vsed by any other."

E. Fischer† has constructed a furnace for obtaining tar from coal-dust, in which the tar is the principal thing.

No doubt the manufacture of tar and ammoniacal liquor for their own sake would be furthered, on the one hand, by a rise in value of the products obtained therefrom, or, on the other hand, by the competition of other systems of lighting (say, that of the electric light), by which the value of lighting-gas would be lowered. No doubt such a state of affairs does not yet exist; there is as yet quite sufficient coal-tar and ammoniacal liquor made at the gas-works for the requirements of industry; and there is every reason for believing that in case of need any amount of the valuable hydrocarbons of gas-tar can be obtained by overheating the residues from the refining of petroleum and paraffin oil. Very successful attempts have also been made to collect the tar and ammoniacal liquor in the coking of coal; and the manufacture of ammonia from the nitrogen of the air is probably only a question of time.

* Wagner's Jahresh. 1865, p. 738.

† Berg- und hüttenmänn. Zeit. xxxix. p. 373.

Hence there seems to be no prospect of an essential rise in price of tar and gas-liquor; neither can the electric light be said to have yet supplanted gas-lighting to any serious degree, at least economically. Nevertheless the conviction seems to be gaining ground among thinking gas-engineers that it is a wrong system, as practised well-nigh universally, to squeeze the maximum quantity of gas out of the coal, and to let the tar come out as it may—that, on the contrary, the most rational system would be to conduct the retort-work so as to obtain tar containing more of the valuable constituents, even if a smaller number of cubic feet of gas were got out (see below). It is to be hoped that this problem will be soonest solved in the enormous gas-works of London and Paris, as these are at the same time among the very largest of all tar-distillers, and consequently are interested in both sides of the question.

Historical Notes on the Applications of Coal-tar and the Products obtained therefrom.

Apart from the proposal mentioned on p. 4, and others equally isolated, for the manufacture and application of coal-tar, it appears that more than a generation elapsed, after the successful introduction of gas-lighting, before the tar, which was obtained therewith from the first, was taken notice of, or at least before it was regarded as a source of profit. Probably at that time the tar was burned as well as possible, a process which is not so simple as it might appear; we shall, later on, describe arrangements which even now are employed for burning tar or heavy tar-oils under certain circumstances. Probably gas-tar has also been employed from the first as a cheap paint for wood and metals, for which purpose it is certainly but little adapted in the raw state, as we shall see later on. But this application and some other occasional ones could only consume a small portion of the coal-tar even then obtained; and the greater portion of it remained a great nuisance to the gas-manufacturers, who had sometimes to pay considerable sums to get rid of it.

The first statements on the nature of the products obtained by the destructive distillation of coal were made by Clayton (1737–38). Towards the end of the last century Lebon (in France) once more drew attention to this subject, and specially pointed out the use of these products for preserving timber.

In Germany the first more extensive employment of gas-tar was for making roofing-felt, for which purpose it has to be deprived of its more volatile constituents. Instead of condensing these, they were at first almost everywhere, and, later on in many cases, removed by evaporating the tar in open vessels, thus creating a considerable danger of fire. In Germany, Brönnert, of Frankfort, was the first (in 1846) to condense the more volatile tar-oils, from which he prepared a detergent, long after known by his name, and consisting principally of benzene.

In England, where the manufacture of lighting-gas originated, and where it has always been, and still is, carried on to a very much greater extent than on the continent of Europe, a more extensive industrial employment for coal-tar was first opened out by the invention of Bethell (1838) for preserving timber, especially railway sleepers, by impregnation with the heavy oil distilled from gas-tar. From that time dates the introduction of tar-distilling on a large scale. The light oils may have been lost even here in some cases; but more usually they were condensed and employed as "coal-tar naphtha" for burning, and for dissolving india-rubber.

The day of the light tar-oils came after A. W. Hoffmann (1845) had shown the presence of benzene in them, but especially when Mansfield (whose researches will be mentioned in detail afterwards), in his patent-specification (1847), for the first time accurately described the composition of those oils, along with a process for preparing benzene in a pure state and on a large scale, and with proposals for utilizing the tar-oils of lowest boiling-point for lighting-purposes. The industrial preparation of benzene was soon followed by that of nitrobenzene, at that time only employed as a substitute for the essential oil of bitter almonds, and known by the French fancy name "essence de Mirbane." But all these applications produced only a limited demand for the light oils which could be made from the rapidly increasing quantities of gas-tar; so that the latter, except in a few instances locally, did not attain any considerable commercial value. But a sudden impetus was given to tar-distilling in 1856 by the discovery of the aniline colours, the material which forms their starting-point, benzol, being exclusively derived from coal-tar.

In the centres of industry, where at the same time most gas is made, coal-tar was at once converted from a nuisance into a commercial article in good demand at good prices. Although only

about one per cent. of the tar is obtained as benzol, this article at first yielded so much that the other products of tar-distilling could be sold at low rates and new markets could be opened out for them. It is true that, as usual, excessive competition led at one time to a great fall in the price of benzol; and as at the same time the sale of creosote oil and pitch was very difficult, tar-distilling seemed to be hardly a remunerative business. But this state of affairs passed away. Even at that time a more rational utilization of the by-products permitted working at a profit; and this, so long as tar is at a reasonable price, was fully secured when, through Graebe and Liebermann's discovery of artificial alizarine, anthracene obtained a much higher value than any other product from coal-tar.

In the course of time the following state of affairs has established itself. In England, where by far the largest quantity of gas-tar is produced, where benzene was discovered by Faraday, its industrial preparation by Mansfield, the first aniline colour by Perkin, and where the conditions are the most favourable for the purchase of the necessary chemicals as well as for the sale of the colouring-matters, the manufacture of artificial dyes has only risen to moderate dimensions. The same has taken place in France. On the other hand, in Germany and Switzerland the manufacture of coal-tar colours has been established on an enormous scale, so that the tar produced there can only supply a small portion of the benzol and anthracene required, the larger portion being imported from England and France, partly in the form of aniline. But the employment of the other coal-tar products, especially dead oil and pitch, in Germany has by no means increased *pari passu* with that of benzol and anthracene; the former, very cheap articles would frequently have to seek a market at such distances that the expense of carriage would become excessive. Moreover gas-making in Germany is only partially concentrated at a few large centres of industry; very many small gas-works are scattered all over the country, sometimes not even situated near a railway line, and hardly ever on the bank of a canal or navigable river; so that the collecting of tar for a larger tar-distillery does not pay. Hence in Germany and Switzerland, just where the manufacture of coal-tar dyes has reached its greatest development, it frequently happens that the tar produced at the gas-works has to be burned under the retorts.

The *quantity of coal-tar* annually produced is estimated by Wurtz* for England at 120,000 to 130,000 tons; for Belgium at 10,000 tons; France at 30,000 to 35,000 tons. The Compagnie Parisienne de l'éclairage au gaz distils annually about 25,000, M. Dehaynin 14,000 tons. Dr. Weyl at Mannheim† puts the figures much higher, viz. at 350,000 tons for all Europe, of which quantity the larger half is produced in England; he sets down France at 50,000, Belgium at 15,000, Holland at 7500 tons. According to Mills‡, in 1874 about ten million tons of coal were used for gas-making in the United Kingdom; this would correspond to the production of at least 450,000 tons of tar.

According to a very reliable estimation in the 'Chemische Industrie,' 1880, p. 324, the amount of tar distilled in Germany is 37,500 tons, from which are produced 175 tons of anthracene, 375 tons of benzol, and 281 tons of solvent naphtha. In Berlin alone, from 300,000 tons of coal, 15,000 tons of tar are obtained.

The Production of Coal-tar at the Gas-works.

Nearly all coal-tar is a by-product of the manufacture of lighting-gas, and is therefore frequently called *gas-tar*. It is not within the scope of this treatise to give a description of the ordinary contrivances for condensing the tar, which belong entirely to the domain of gas-making. It is sufficient to mention that the constituents of the tar escape from the gas-retorts in the form of vapour, possibly along with a little solid free carbon in an extremely finely divided state. They are precipitated in the hydraulic main, the condensers, scrubbers, &c. in a liquid state at the same time as the ammoniacal liquor (gas-liquor) is formed. But this is the proper place to show how much the quantity, and to a much greater extent the quality, of the tar is influenced by the *temperature* at which the decomposition of the coal is carried on. If the temperature be a comparatively low one, mostly such hydrocarbons are formed as belong to the paraffin (methane) series, having the general formula C_xH_{2x+2} . The lower members of this series are liquid, and, furnished in the purified state, are lighting and lubricating oils; the higher ones

* *Matières colorantes artificielles*, 1876, p. 13.

† Private communication.

‡ *Destructive Distillation*, p. 26.

are solid and form paraffin. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen of hydroxyl:—*e.g.* cresol, $C_6H_4(CH_3)(OH)$; guaiacol, $C_6H_4(OH)(OCH_3)$; creosol, $C_6H_3(CH_3)(OH)(OCH_3)$, &c. Liquid products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. The hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane or marsh-gas, CH_4 , and free hydrogen as principal constituents, and is very much increased in quantity. The carbon thus set free is partly deposited in the retorts themselves, and then occurs in a very compact graphitoid form; another portion of the free carbon occurs in a state of extremely fine division in the tar, and forms a constituent of the pitch or coke remaining behind from tar-distilling; another portion contributes to the formation of compounds richer in carbon, belonging to the "aromatic" series, all of which are derived from benzene, C_6H_6 . At the same time the action of heat effects further molecular "condensations," usually with separation of hydrogen, by which process compounds of a higher molecular weight are formed, as naphthalene, anthracene, phenanthrene, chrysene, &c. The never absent oxygen must also in this case cause the formation of phenols; but here phenol proper, or carbolic acid, $C_6H_5(OH)$, predominates, whilst cresol and the other homologues are diminished in quantity, and the bioxy-benzenes, as well as their methylated derivatives, disappear altogether.

The above will be better illustrated by the statement* that Zwickau glance coal yielded the following quite different products, according to whether it was put into a cold retort and gradually brought to a red heat (*a*), or distilled quickly from a very hot retort (*b*):—

* From Stohmann-Kerl's 'Chemie,' 3rd ed. vi. p. 1162.

21

	<i>a.</i>	<i>b.</i>
Coke.....	60	50
Water	10·7	7·7
Tar	12	10
Gas and loss.....	17·1	82·1

The tar from *a* consisted of photogen, paraffin oil, lubricating-oil, paraffin, and creosote; that from *b*, of benzene, toluene, naphthalene, anthracene (together with heavy oils corresponding to the paraffin and lubricating-oil), and much creosote.

The same cause explains the difference between the tar of wood-gas-works, that of wood-vinegar-works, and that of charcoal heaps. The former, produced at a very high temperature, is black, thin, smells almost like coal-tar, and contains much real phenol, along with benzene, toluene, naphthalene, &c. The tar obtained at a lower temperature, especially that from the charcoal heaps, contains mostly cresol and guaiacol in the place of phenol, and paraffin instead of naphthalene; it has a lighter brown colour and a much milder smell.

¶ A further difference between distillation at high and at low temperatures is stated to consist in the fact that most of the nitrogen appears in the former case in aniline and fatty amines (ethylamine, propylamine, amylamine), in the latter case in bases of the pyridine series, along with picoline, lutidine, viridine, &c. But this requires to be verified by more detailed investigations.

Of course it is not possible to get the above products in any desired quality from any one of the raw materials here concerned, merely by altering the temperature of the dry distillation. It is, for instance, doubtful whether real benzene can be obtained at all by direct distillation from younger fossils, as peat, browncoals, some sorts of bituminous shales, &c.; and in no case can they serve for a profitable extraction of benzene and the other aromatic hydrocarbons. On the other hand, photogen, paraffin oil, &c. cannot be profitably made from coal by distillation at a lower temperature*; for cases like that of the Zwickau coal, mentioned above, do not furnish a rule for industrial practice, which has proved that even among

* Professor Dittmar, of Glasgow, informs me that, twenty years ago, at Manchester, oils of the formula C_nH_{2n+2} were made by the distillation of coal at a low temperature. But no doubt this was cannel coal, which in that respect occupies a place between real coal and younger fossils.

browncoals only certain light, earthy descriptions ("Schweelkohle") are adapted for the manufacture of lighting-oils. But we shall see that it is at least in our power, by *subsequent overheating*, to split up the fatty products (paraffins) from browncoal and petroleum, to a great extent, into gases and aromatic compounds.

Our present task lies only with the treatment of real coal. We must remember that at a lower temperature less permanent gases and more methylated derivatives (toluene, xylene, higher phenols), at a higher temperature more gases, along with benzene, naphthalene, anthracene, and far more free carbon, are formed. At very high temperatures the tendency to complete dissociation becomes far more pronounced; the products approach more and more free carbon on the one hand, and free hydrogen on the other; but this end itself is never actually reached at the temperatures attainable to us. Most gas-engineers try above everything to get as much gas as possible out of the coal, and therefore distil at the highest possible temperature. Up to a certain point this is quite rational, and is even unavoidable from the nature of the material now universally employed for gas-retorts, viz. fireclay. This point seems to be reached when the fatty compounds are split up as far as possible, before any considerable separation of free carbon has taken place. Beyond this point more gas will be got; but its lighting-power will be less; the tar will at first contain a little more of the valuable anthracene, but at the same time even more of naphthalene, which has much less value, and of phenanthrene, pyrene, chrysene, diphenyl, &c., which are quite valueless; so that its value on the whole will be less. The separation of free carbon in the retorts and the tar is also largely increased. In England the usual temperature of working seems now to be about 1100° C. (=2000° F.). But, properly speaking, it should be experimentally ascertained, and that for every class of gas-coal specially, at what temperature the maximum of lighting-power is obtained, even if concentrated in a smaller volume of gas, and at what temperature a maximum yield of benzene, toluene, phenol, and anthracene in the tar. Probably the two maxima will not coincide; and it will then be a matter of business calculation whether the one or the other is to be worked for. It is evident that the market prices of the tar products will influence this consideration largely, and that any diminution in the price of gas will turn the scale in favour of richer tar.

Some statements on the influence of the *shape* of the gas-retorts

and exit-pipes on the quality of the tar have been made by Hayes*. If the shape of the retorts be such that the volatile products are carried away from the hottest place through a narrow pipe, much less heavy and much more light oil is said to be obtained; the coke is then much more compact and harder. Even a slight modification of the width of the pipe is said to influence the nature of the products.

That the difference of quality of the coal influences the quantity of valuable constituents of the tar, is a matter of course. It is especially injurious to the quality of the tar, if the lighting-power of the gas is augmented by addition of *boghead* or any similar *bituminous shales* to the coal. In such a case, even at the highest practical temperature, hydrocarbons of the paraffin series appear more extensively in the tar. The benzol will contain hydrocarbons similar to petroleum-spirit, and the anthracene paraffin, neither of which impurities can be removed by the methods usually practised, viz. fractional distillation or crystallization. Hence many tar-distillers stipulate in their contracts that the gas-works must not mix more than 5 per cent of shale (*boghead* &c.) with their gas-coal.

Besides paraffins, *boghead* tar contains principally toluene and naphthalene, and but little benzene and anthracene. The real *boghead*, or *Torbanehill* mineral, is now practically exhausted; but the name is still used in commerce for shales of much inferior value. The shale-spirit got from these contains, along with the paraffins, very sensible quantities of benzene and toluene†.

Through the kind mediation of Professor Dittmar I have received the following information from Dr. Ronalds on the tar from *cannel coals* and *boghead*. Scotch cannel were exclusively used in Edinburgh and Leith, and probably in most parts of Scotland, for making gas prior to the coal famine in 1851–53, when many companies took to using common splint coal, and some attempts were even made to use shale mixed with coal. Shales give little or no tar; and the naphtha (if *any*) is similar to that from *boghead* (the hydride series). The quality of the tar now made from the various kinds of *cannel coal* (such as those from Lismahago, Marquis of Lothian, Arnichar, Benhar, Walleford, and numerous other localities) is very different from that obtained formerly. Twenty years ago, when

* Silliman's Amer. Journal, March 1859.

† Watson Smith, private communication.

low heats were used at the gas-works, as much as 8 per cent. of naphtha, i. e. benzene and its homologues, was obtained by distillation with steam. This diminished slowly as the heat employed at the gas-works increased, until it had fallen a few years ago to about 3 per cent. The naphtha from Scotch tar was always rich in toluene, and contained less benzene than that from ordinary bituminous coal. It contains little naphthalene and very little anthracene—so little of the latter that its extraction is not worth while. It also contains considerable quantities of paraffins, but mostly of low melting-points. Naphthalene and paraffin seem to go together; wherever there is much of the one, the other is almost always present too. When shale or boghead or similar semicoals are mixed with cannel or bituminous coal, the light naphtha is a mixture of the benzene and of the hydride (methane) series; as these are very difficult to separate, the benzols are comparatively valueless as commercial products. The heat used in the making of the gas and tar appears to have quite as much, if not more, to do with the quality of the products as the quality of the coal.

The total yield of tar from the coal may be set down on the average as 5 per cent. on the weight. According to Wurtz*, St.-Etienne coal only yields 4 per cent. of poor tar, but Anzin and Mons coal 6·73 per cent., and "Prussian" coal up to 7 per cent., of rich tar. Of the German coals those from Upper Silesia yield the best, those from Westphalia the poorest tar. The yield of tar is given in the Table† (p. 14), which shows that from various descriptions of coal, along with that of other products, on the average there is obtained

	Tar.	Ammoniacal liquor.
from coal generally	4 to 6	6 to 10 per cent.
„ English coals	4·5	6 „ „
„ Silesian „	5 to 6	9 „ „

* Dictionn. de Chimie, i. p. 1631.

† Stohmann-Kerl's Chemie, 3rd ed. iv. p. 624.

1 ton (2240 lb.).	Gas.		Coke.	Tar.	Gas-liquor.	Loss.
	cubic feet.	lb.	lb.	lb.	lb.	lb.
Boghead cannell.	13334	...	715	733.3
Newcastle	9833	...	1428	98.3	60	...
Wigan cannell	10850	...	1332	218.3	161.6	...
Lochgelly	8331	...	1245	225	340	...
$\frac{1}{2}$ Lochgelly + $\frac{1}{2}$ boghead	9055	...	1200	400	170	...
$\frac{1}{15}$ " + $\frac{1}{15}$ "	9050	...	1205	335	290	...
$\frac{1}{11}$ " + $\frac{1}{11}$ "	9750	...	1240	227	270	...
Pelton Main (Durham)	9500	...	1540	112.5	112.5	...
$\frac{1}{2}$ " + $\frac{1}{2}$ boghead	12800	...	1366	206.6	116.6	...
Lismahago cannell, I. ...	11681	461	1091	594	4.5	87.5
" " " II.	9878	483.5	1064	603	4.5	85
Ramsay's Newcastle cannell	9016	410	1435	295	6.7	93.3
Derbyshire deep-seam ...	9400	300	1335	219	179	207
Wemyss cannell, I.	10976	551	1124.5	224	...	340
" " " II.	10192	528	1188	197	...	327
Wigan cannell	9408	338	1326	250	...	326

Tar as a By-product in Coke-making.

Possibly in future a large supply of tar will be offered as a by-product from the coking of coal for metallurgical purposes. The tar formed in this operation is as yet burnt in most places, either quite uselessly at the furnace-mouth, or, in a more rational way, so as to aid in the heating of the coke-ovens. It is the usual opinion that any condensation of tar and ammonia in coke-making injures the quality of the coke; but in some quarters it has always been asserted that this drawback can be avoided by a proper mode of proceeding, and that it is quite possible to obtain coke of excellent quality, fit for blast-furnaces or any other metallurgical purpose, along with tar, ammoniacal liquor, and even illuminating-gas. Already in 1768 a chemist named Stauff, at Fischbach near Saarbrücken, obtained tar by making coke in muffle furnaces*. One of the oldest apparatus of this kind (1856) is that of Knab, which had, however, to be considerably modified in order to be fit for real work. According to a description dating from 1862† such a modified system was very successfully at work at St. Etienne. The gases and other products escaping from the closed coke-ovens were passed into a hydraulic main, cooled by air, where tar and ammonia con-

* De Gonsanne, quoted in Gurlt, Steinkohlenbriquettes, p. 22.

† Gaultier de Claubry, Bulletin de la Société d'encouragement, 1862, p. 581.

densed, while the gases were continually drawn off by exhausters and employed for heating the coke-ovens, by issuing from an annular burner along with air admitted into its inner space. In order to collect the condensable products more completely, the gas is first passed through coke-scrubbers fed with water, and then through a set of 500 upright lead pipes of $\frac{3}{8}$ inch width, externally cooled by water. There were said to be obtained :—

Large coke	70.00	per cent.
Small „	1.50	„
Breeze „	2.50	„
Graphite	0.50	„
Tar.....	4.00	„
Ammoniacal liquor	9.00	„
Gas	10.58	„
Loss	1.92	• „
	<hr/> 100.00	

Further modifications of Knab's process have been carried out at Bessèges, and have been minutely described by Dr. Angus Smith*. According to his information each oven produced per annum :—

	1874.	1875.
	tons.	tons.
Coke.....	390.000	405.880
Tar	10.621	9.336
Sulphate of ammonia ...	2.134	1.594

The coals are said to yield 73 or 74 per cent. of coke. The temperature in the ovens at charging is 443° to 495° , after 72 hours 760° to 880° , in the flues up to 905° C.

The report reproduced by Dr. Smith seems to be rather too favourable when it is compared with the following authentic information on the working of the ovens at Bessèges and Terrenoire in 1879†.

* Alkali Acts, 14th and 15th Annual Reports, for 1877 and 1878, p. 49 *et seq.*

† Private communication from Mr. A. Hüssener, Essen.

Blackwell's patent (1861) seeks to obtain considerable quantities of very rich tar and (but weak) ammoniacal liquor, even when the coal is coked in heaps, by simple contrivances. A similar patent had been taken out previously by Jones; but nothing is known of any great success of either.

In 1870 the Berlin Society for the advancement of industry offered a prize for a coke-oven which should prove by practical trials to condense the volatile products in an economical way, while furnishing the best blast-furnace coke. This prize has not yet been awarded.

A recent German patent of Ströhmer and Schultz* proposes to draw off the gases and vapours from coke-ovens by a sliding tube before they have time to be decomposed by the heat of the brick-work. Lest the quality of the coke should suffer by the gases being drawn off too fast, the sliding tube is raised or lowered by an automatic pressure-regulator.

The tar obtained from Knab's or Pauwel's ovens, or in any other way where hard coke is the principal product, differs to some extent in composition from the ordinary gas-retort tar—and quite naturally, since in the former case the temperature has been much lower. Behrens† distilled the same kind of coal in fireclay retorts and Pauwel's ovens, in order to examine the influence of temperature on the formation of tar. The retort tar contained much more benzene and toluene, but also much more naphthalene and other solid substances; the oven tar was specifically lighter, and consisted principally of liquid hydrocarbons. The latter contained much more acids than the former; but among them real phenol (carbolic acid) was almost absent. Also Wurtz (*l. c.*) states that oven tar contains less benzene and carbolic acid, but more toluene and higher phenols than gas-tar. Hence the assertion that oven tar is more valuable than gas-tar would seem to be quite erroneous; it may possibly have been caused by the great fluidity of oven tar. This appears to be confirmed by the observation‡ that after the coke-ovens had been improved and their temperature raised, the tar became richer in benzene.

* No. 8174, dated May 27, 1879.

† Dingler's Journ. ccviii. p. 361.

‡ Gaultier de Claubry, *l. c.*

RECOVERY OF THE TAR SUSPENDED IN THE GAS.

A further source of tar, or rather of some of its most valuable portions, seems to be indicated by the attempts, partly crowned with success, to deprive ordinary illuminating-gas, by a special treatment, of the tarry particles suspended in the gas like a fine mist or even contained as real vapour. These particles are to some extent precipitated in the gas-pipes, and are found both at the gas-works and in the "siphons" of the street pipes as oils or as masses of crystallized naphthalene. These oils have been examined in detail by Gasch *. He found that they gave off

3-6 per cent.	up to	100°	
5-8	„	from 100 to	130°
5-15	„	130	„ 150,
19-36	„	150	„ 180,—

in the whole, 47-76 per cent. up to the point where naphthalene appeared. They contain numerous sulphur compounds—below 100° carbon bisulphide, above 100° probably mercaptanes. An exact examination of these oils (which do not appear to be systematically collected anywhere) is yet wanting.

The quantity of tar can be considerably increased by supplementing the condensing action of the air-condensers and scrubbers by more efficient apparatus. This is the object of the process of Pelouze and Audouin †, which is being worked very successfully at Paris. That they are not the real inventors of the process, has been proved to conviction by Colladon ‡. The invention proceeds from the principle that mere cooling cannot possibly condense all the tar, because the latter remains mechanically suspended in the gas in the shape of extremely minute liquid drops, *i. e.* in the form of a mist. A portion of this is retained in the coke-scrubbers, but very far from all of it. The result is different when the gas is made to issue through narrow apertures and impinge against a broad solid surface, over which it must spread. The fine liquid particles are thus brought into very much increased contact with each other and with solid bodies, gather into larger drops, and are thus retained. Fig. 1 shows how this principle is carried out. The gas passes into a vessel A through the inlet-pipe B, and leaves it at C.

* Journal für Gasbeleuchtung, 1873, p. 65; Wagner's Jahreshb. 1873, p. 914.

† Compt. Rend. lxxvi. pp. 264, 928.

‡ Ibid. lxxvii. p. 819.

Fig. 1.

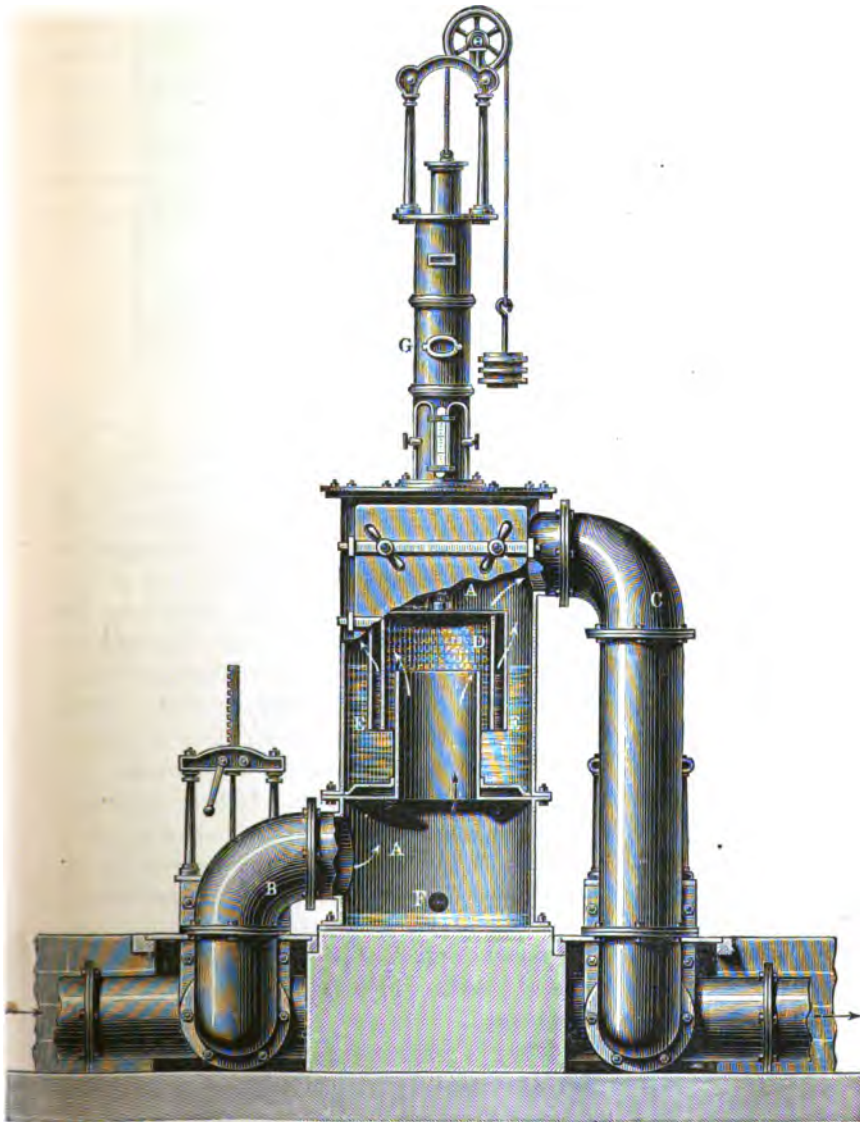
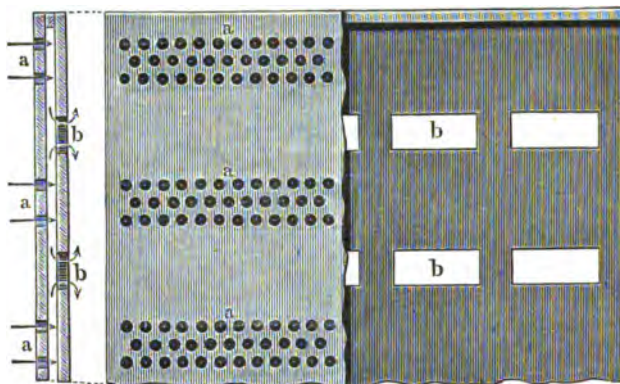


Fig. 2.



Inside A is a cylinder D, the proper purifying-apparatus, which floats in the hydraulic tar lute E, so that the gas can only get from B to C through the perforated sides of D. The latter are made of three concentric sheets of brass, $\frac{1}{16}$ inch apart, and perforated with many holes. The holes *a a* (fig. 2) are $\frac{1}{16}$ inch wide, arranged in three rows, placed transverse to each other, so that the jets of gas, issuing through the holes of the innermost plate, meet with the solid portion of the middle plate, and when issuing through the holes of the latter again meet solid portions of the outermost plate, from which at last they can get into the upper space of B. Since experience has shown that the holes of the middle plate especially are readily clogged up with tar, the apertures of this plate are now made (as shown in fig. 2) larger and square. It has also been attempted to replace the holes by vertical slits, which do not so easily get stopped up. The tar condensed by the impact on the plates runs into the tar-cistern E, flows over and runs away at F. Since of course some pressure is lost in this apparatus, it is necessary to let the gas, previously well cooled, issue under a certain surplus pressure, say $1\frac{3}{4}$ – $1\frac{7}{8}$ inch, which is kept constant by the automatic regulator G.

In 1876 there were eight such condensers at work in Paris, which produced:—at the Ternes works, from each 1000 cubic metres of well-cooled gas, 9 kilog. of tar; at the La Villette works, from 1000 cubic metres of gas not so well cooled, as much as 72 kilog. of tar, and 16 litres of liquor containing 80 grams of ammonia per litre.

The tar is much lighter than ordinary gas-tar; it yields 20 per cent. of light oils, instead of 3 to 5 per cent.

The same apparatus is said to be employed at many other French works. It has also been tried in Germany, but has not made its way there, probably because the undoubted efficiency of its principle is defeated by the difficulty of keeping the holes from being clogged up, and because it is as yet doubtful whether the extra yield of tar is not counterbalanced by the certain loss in the illuminating-power of the gas.

The gas can be even more completely deprived, not merely of the mechanically suspended tar but even of the benzol vapour which it contains, by passing it through *liquid absorbents* for those substances. One of the first attempts in this direction was made by A. Vogel*, who passed the gas through colza oil. The weight of the oil was increased 20·5 per cent.; its illuminating-power was very much increased; and that of the gas did not suffer (?). The process did not aim at obtaining benzol as such; but this was the case with the patent taken out by Lake for Caro, A. Clemm, K. Clemm, and Engelhorn†. They proposed bringing the gas into contact with oils of high boiling-point, such as petroleum, paraffine oil, or fatty oils, and to separate the benzene, toluene, &c. absorbed by those oils, by subsequent fractional distillation; the residual oil was to be used over again as an absorbent. Evidently the illuminating-power of the gas must be much reduced by such treatment. It is now generally assumed‡ that the presence of benzene vapour in gas is most important in this respect; and it is doubtful whether its replacement by the vapours of petroleum spirit &c. would be practicable on a very extended scale.

In any case, although a good deal of benzene could be obtained by the above-mentioned patent, it did not hold its ground for any length of time.

PREPARATION OF AROMATIC HYDROCARBONS *by decomposing fatty compounds of high boiling-points.*

Although we are not directly concerned with it, we shall briefly mention the attempts at obtaining the important constituents of coal-tar (so to say, artificial coal-tar) by decomposing the heaviest

* Dingler's Journal, cliii. p. 464.

† Dated Feb. 17, 1869.

‡ Compare especially Berthelot, Compt. Rend. lxxxiv. p. 571.

oils, otherwise hardly of any practical use, of the petroleum and paraffine-oil refineries. It has been known for some time that such oils, consisting essentially of paraffines (C_nH_{2n+2}) and olefines (C_nH_{2n})—at any rate, of “fatty” substances—yield substances belonging to the aromatic series by molecular condensations, when heated to a very high temperature, *e.g.* when they are passed through red-hot tubes. More exact experiments to ascertain how far this reaction might be applicable on a practical scale were called forth by a prize offered in 1877 by the Berlin Society for the Promotion of Industry. It was required to be shown that converting the high-boiling oils of the browncoal-tar, by a technically applicable process, into the hydrocarbons forming the basis of the aniline-colour and alizarine industry is possible.

Liebermann and Burg* found that the above oils, when passed through red-hot tubes filled with porous material, are converted into a mixture of hydrocarbons very similar to coal-tar, containing about 4 per cent. benzene and toluene and 0.9 per cent. crude anthracene. Petroleum and vulcan oil yielded much gas and benzene, but hardly any anthracene. Coal-tar oils, boiling between 140° and 150° and between 150° and 210° , when treated in a similar way, suffered much less loss of weight. The quantitative results obtained by those chemists are, from their own showing, no guide as to those obtainable on the large scale, for which special experiments would be required. Similar to the above were the results of Salzmann and Wichelhaus†; and Attenberg‡ proved the same for wood-tar. The most extended paper on this subject has been published by Letny§. He examined a tarry condensate, produced in the manufacture of gas by passing heavy petroleum “tailings” through red-hot tubes filled with wood; after several passages through the retort he found it entirely similar to coal-tar, and especially proved it to contain benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, along with unchanged petroleum. After this he tried passing the petroleum-tailings on a small scale through a red-hot tube filled with charcoal. He obtained 33.3 per cent. of gas and 66 per cent. of tar, containing much amylene, benzene, toluene, xyene, and higher-boiling oils, but no solid hydro-

* Ber. deutsch. chem. Ges. 1878, p. 723.

† Ibidem, pp. 802 and 1431.

‡ Ibidem, p. 1222.

§ Dingler's Journal, ccxxix. p. 353.

carbons. The absence of the latter is ascribed by Letny to the comparatively small thickness of the layer of red-hot charcoal which the petroleum vapours had to pass on the small scale. At a higher pressure more oils of low boiling-point were formed, but on the whole less tar and bad gas. The raw material for these experiments is the residue from refining the petroleum of Baku in South Russia, which, like that of North-American petroleum, can be had in any quantity.

Rudnew* reports that at the Kasan gas-works the tar from making petroleum-gas is already distilled in the ordinary way, and yields 10 to 12 per cent. benzol, and up to 5 per cent. naphthalene; anthracene is also always present, and is to be recovered as well. It is worthy of notice that such tar is all but free from phenols—very naturally, as the raw material contains little or no oxygen.

* Dingler's Journal, ccxxxix. p. 72.

CHAPTER II.

THE PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS.

COAL-TAR is a black, more or less viscid fluid of peculiar smell, of specific gravity 1·1 to 1·2, usually between 1·12 and 1·15*. It has been asserted by some that tar is more valuable the lower its specific gravity. In any case this could only be said of pure coal-tar; but since the tar from cannel coal, shale, &c., which contains more toluene and paraffine than coal-tar, is much lighter than the latter, the above criterion is not in any way to be depended upon.

Coal-tar is an extremely complex mixture of chemical compounds, some of which have not even been isolated as yet. Thus very little is known of the indifferent oils, occurring in its distillation, between the phenols and naphthalenes on the one side, and anthracene oil on the other; neither do we know all the compounds existing in crude anthracene, and still less those constituting the pitch.

Since tar always contains a considerable quantity of ammoniacal liquor mechanically mixed with it, we must expect to find all the constituents of the latter in the tar; also those of the gas probably all occur in it, being absorbed by it.

The following is an enumeration of the compounds hitherto found in coal-tar or reasonably presumed to exist in it; they will afterwards be described in detail.

* It is strange that authors like Bolley, Wurtz, Girard and Delaire, Vincent, and others have stated the specific gravity of coal-tar to be equal to or below that of water. Evidently there has been confusion with tar from browncoal or bog-head &c.; and a wrong quotation of this kind has travelled from one book to another without criticism.

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS.			
I. <i>Methane Series</i> , C_nH_{2n+2} .			
Methane	CH_4		
Ethane	C_2H_6		
Propane	C_3H_8	-20
Butane (normal)	C_4H_{10}		+ 1
Pentane (normal)	C_5H_{12}	liquid	37-39
Isopentane	C_5H_{12}	"	30
Hexane (normal)	C_6H_{14}	"	69-71
Heptane (normal)	C_7H_{16}	"	98
Ethylisoamyl	C_7H_{16}	"	90-3
Octane, I.	C_8H_{18}	"	119-120
" II.	C_8H_{18}	"	124
Nonane, I.	C_9H_{20}	"	130
" II.	C_9H_{20}	"	150-8
Decane, I.	$C_{10}H_{22}$	"	158-161
" II.	$C_{10}H_{22}$	"	170-171
Undecane	$C_{11}H_{24}$	"	180-182
Duodecane	$C_{12}H_{26}$	"	200-202
Tredecane	$C_{13}H_{28}$	"	218-220
Quatuordecane	$C_{14}H_{30}$	"	236-240
Quindecane	$C_{15}H_{32}$	"	258-262
Sedecane.....	$C_{16}H_{34}$	"	280
Paraffins	$C_{17}H_{36}$ to $C_{27}H_{56}$	40-60	
II. <i>Ethylene Series</i> , C_nH_{2n} .			
Ethylene	C_2H_4	-110
Propylene	C_3H_6	"
Butylene (normal).....	C_4H_8	- 5
Pseudobutylene	C_4H_8	+ 1
Isobutylene.....	C_4H_8	- 8
Amylene	C_5H_{10}	liquid	+ 39
Hexylene.....	C_6H_{12}	"	68-70
Heptylene	C_7H_{14}	"	96-99
III. <i>Addition-products of the Benzene Series</i> , C_nH_{2n} .			
Hexahydrobenzene.....	C_6H_{12}	liquid	69
Hexahydrotoluene.....	C_7H_{14}	"	97
Hexahydroisoxylene	C_8H_{16}	"	118
IV. <i>Acetylene Series</i> , C_nH_{2n-2} .			
Acetylene	C_2H_2		
Crotonylene	C_4H_6	liquid	18
Hexoxylene.....	C_6H_{10}	"	80
Higher members	$C_{12}H_{22}$	"	210
"	$C_{14}H_{26}$	"	240
"	$C_{16}H_{30}$	"	280
V. <i>Series</i> C_nH_{2n-4} .			
Nonone	C_9H_{14}	liquid	174

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS (<i>continued</i>).			
		° C.	° C.
VI. <i>Benzene Series</i> , C_nH_{2n-6} .			
Benzene	C_6H_6	4.5-7	80.4
Toluene	C_7H_8	liquid	111
Xylene.....	C_8H_{10}	"	
Orthoxylene	"	141-143
Metaxylene	"	137-138
Paraxylene	15	136-137
Pseudocumene	C_9H_{12}	"	165-166
Mesitylene	C_9H_{12}	"	163
VII. <i>Styrolene</i>			
Hydride of styrolene (?)	C_8H_8	"	145
.....	C_8H_{10}	"	
VIII. <i>Naphthalene</i>			
Naphthalene dihydride.....	$C_{10}H_8$	79	217
.....	$C_{10}H_{10}$	liquid	200-210
" tetrahydride	$C_{10}H_{12}$	"	190
Methylnaphthalene	$C_{11}H_{10}$	-18	242
IX. <i>Acenaphthene</i>			
Acenaphthene hydride	$C_{12}H_{10}$	100	285
.....	$C_{12}H_{12}$	260
Diphenyl.....	$C_{12}H_{10}$	70.5	254
Fluorene.....	$C_{13}H_{10}$	113	295
<i>Anthracene</i>	$C_{14}H_{10}$	213	360
Anthracene dihydride	$C_{14}H_{12}$	106	305
" hexahydride	$C_{14}H_{16}$	63	290
Methylanthracene	$C_{15}H_{12}$	208-210	
Dimethylanthracene (?)	$C_{16}H_{14}$	224-225	
Phenanthrene.....	$C_{14}H_{10}$	99-100	340
Pseudophenanthrene (?)	$C_{16}H_{12}$	115	
Synanthrene (?)	$C_{14}H_{10}$	189-195	
Fluoranthene	$C_{15}H_{10}$	109	
Pyrene.....	$C_{16}H_{10}$	142	above 360
Chrysene.....	$C_{18}H_{12}$	245	440
Chrysogene.....	280-290	
Retene.....	$C_{18}H_{18}$	98-99	350
Succisterene ?.....	160-162	above 300
Picene.....	$C_{22}H_{14}$	345	
Benzerythrene	$C_{24}H_{18}$	307-308	
Bitumen.			
B. OXYGENIZED COMPOUNDS.			
Water	H_2O	0	100
Methylic alcohol (?).....	CH_3O	liquid	63
Ethylic alcohol (?)	C_2H_5O	"	78.5
<i>Acids and Phenols.</i>			
Acetic acid	$C_2H_3O_2$	16	119
Phenol (carbolic acid)	C_6H_5O	42	184
Orthocresol.....	C_7H_7O	31	185-186
Paracresol	"	36	198
Metacresol	"	liquid	195-200

	Formula.	Melting-point.	Boiling-point.
B. OXYGENIZED COMPOUNDS (continued).		° C.	° C.
<i>Acids and Phenols (continued).</i>			
Xylenols: Ortho 1, 2, 4	$C_8H_{10}O$	61	225
Meta 1, 2, 3	"	73	216
Meta 1, 3, 4	"	liquid	211-5
Para 1, 3, 4	"	74.5	211-213
Rosolic acid	$C_{19}H_{14}O_8$?	
Brunolic acid (?)			
C. SULPHURETTED COMPOUNDS.			
Hydrogen sulphide	H_2S		
Ammonium sulphide	$(NH_4)_2S$		
Ammonium sulphocyanide	$(NH_4)NCS$		
Sulphur dioxide	SO_2		
Carbon bisulphide	CS_2	liquid	47
" oxy-sulphide	OOS		
Mercaptanes			
Alliol (?)			
D. NITROGENIZED COMPOUNDS.			
I. Basic.			
Ammonia	NH_3		
(Ammonium compounds mentioned under C.)			
Methylamine, ethylamine, &c.		liquid	
Cepitine	$C_5H_{13}N$	"	95
Aniline	C_6H_7N	—8	182
Pyridine	C_5H_5N	liquid	116.7
Picoline	C_6H_7N	"	135
Lutidine	C_7H_9N	"	154.5
Collidine	$C_8H_{11}N$	"	179
Parvoline	$C_9H_{13}N$	"	188
Coridine	$C_{10}H_{15}N$	"	211
Rubidine	$C_{11}H_{17}N$	"	230
Viridine	$C_{12}H_{19}N$	"	251
Leucoline	$C_9H_{13}N$	"	238
Iridoline	$C_{10}H_{15}N$	"	252-257
Cryptidine	$C_{11}H_{17}N$	"	274
Acridine	$C_{12}H_9N$	107	360
II. Not Basic.			
Pyrrrol	C_4H_5N	liquid	133
Methylic cyanide	CH_3CN	"	77
Carbazol	$C_{12}H_9N$	238	355
Phenyl-naphthyl-carbazol	$C_{18}H_{11}N$	330	above 440
E. FREE CARBON	C		

HYDROCARBONS OF THE METHANE SERIES, C_nH_{2n+2} .

These hydrocarbons are sometimes called hydrides of monad radicals—also paraffines, because a mixture of the higher solid members of the series, as obtained in the distillation of shale &c., had obtained that name from its great resistance to chemical reactions (*parum affinis*). This mixture, however, contains also non-saturated hydrocarbons (olefines).

The compounds of this series are principally formed in the destructive distillation of wood, peat, shale, browncoal, bog-head, cannel coal, &c., and from coal also when distilled at a comparatively low temperature. Most descriptions of natural petroleum consist of a mixture of all the members of this series. In coal-tar they play a subordinate part; but if, in gas-making, coal has been partly replaced by browncoal, shale, cannel coal, &c., the tar is much richer in fatty hydrocarbons and may easily contain so much of them that the extraction of the aromatic hydrocarbons does not pay.

The compounds of this class are distinguished from the non-saturated hydrocarbons (the ethylene and acetylene series) by not being absorbed by sulphuric acid or bromine; this behaviour can be utilized for separating the two classes. From benzene and its homologues they are distinguished through being hardly at all acted upon by nitric acid in the cold, and not forming nitro-compounds.

The lowest members, up to butane, are at the ordinary temperature gaseous, but may occur in tar in a state of solution, all the more readily as they are easily soluble in ether and alcohol, and thus probably also in benzene &c. The members from pentane upwards are liquid; up to decane they have been observed in tar. The highest members, beginning from $C_{18}H_{38}$, are solid, and form paraffine proper: whether this occurs in tar obtained exclusively from ordinary coal is doubtful.

Methane, CH_4 .

Synonyms—methylic hydride, marsh-gas, fire-damp, light carburetted hydrogen. A colourless gas, devoid of smell or taste. Sp. gr. 0.5566 (air=1). At $0^\circ C$. 100 vols. of water absorb 5.45 vols.; alcohol nearly half its volume. It burns with a pale yellow flame. Passed through red-hot tubes it yields acetylene, benzene, naphthalene. Mixed with air it gives very explosive mixtures.

Ethane, C_2H_6 .

Syn. dimethyl, ethylic hydride. A gas without colour or smell; sp. gr. 1.075; condenses at 4° to a liquid under a pressure of 46 atmospheres. Water dissolves at 0° 9.45 per cent. by volume, alcohol $1\frac{1}{2}$ times its volume. Burns with a bluish, nonluminous flame.

Propane, C_3H_8 .

Syn. propylic hydride. A gas, condensing to a liquid below -20° C.; alcohol dissolves six times its volume.

Butane, C_4H_{10} .

Syn. diethyl, butylic hydride. Two isomers are possible and known; only normal butane, however, $CH_3-CH_2-CH_2-CH_3$, has been found in mineral oils. Sp. gr. 2.01 (air=1). Authorities differ widely as to its boiling-point. Frankland puts it at -23° ; Butlerow at $+1^\circ$, and, under pressure of $2\frac{1}{2}$ atmospheres, at $+18^\circ$. In water it is next to insoluble. Alcohol at 14° C. and 745 millim. pressure dissolves 18.13 vols. It burns with a strongly luminous flame.

Pentane, C_5H_{12} .

Syn. amylic hydride. Of the three isomers the normal and isopentane, $CH_3-CH_2-CH(CH_3)_2$, have been found in cannel and boghead tar. Schorlemmer found in coal-tar only normal pentane.

Normal pentane boils at from 37° to 39° C., sp. gr. at $18^\circ=0.6263$ (water=1). Isopentane boils at 30° , sp. gr. at $18^\circ=0.628$. Both are colourless, very mobile liquids, something similar to chloroform, miscible with ether and alcohol in every proportion, solvents for fats; they burn with a brilliant white flame.

Hexane, C_6H_{14} .

Syn. caprylic hydride. Five isomers; the normal one occurs in petroleum, bog-head, and cannel tar; it is the principal constituent of the most volatile petroleum-ether (gasoline). Boils at $69-71^\circ$; sp. gr. at $17^\circ=0.663$. Colourless, mobile liquid, of faintly ethereal smell, insoluble in water, miscible with ether, alcohol, acetone, &c. (this solubility holds good for all the higher members as well). Burns with a bright, luminous flame.

Warren found another hexane in petroleum, boiling at $61^\circ.3$, which Schorlemmer could not discover in the same.

Heptane, C_7H_{16} .

Syn. cenanthylic hydride. Nine isomers possible. The different tars contain the normal one, boiling at 98° , sp. gr. at $0^\circ = 0.7006$, at $15^\circ = 0.6886$; also ethylisoamyl, boiling at 90.3° , sp. gr. at $0^\circ = 0.6969$. Mobile liquids, of faint, pleasant smell; burn with a little smoking flame.

Octane, C_8H_{18} .

Syn. caprylic hydride, dibutyl, valyl. Of the eighteen possible isomers one boiling at 119° or 120° (sp. gr. at $17^\circ = 0.719$), and another, probably the normal one, boiling at 124° (sp. gr. at $0^\circ = 0.7188$), have been found in petroleum, boghead-, and coal-tar. They are limpid liquids with an ethereal smell and somewhat burning taste. The ordinary petroleum-spirit (ligroine) of commerce contains principally heptane and octane.

Nonane, C_9H_{20} .

That found in petroleum boils according to Wurtz at $130-132^\circ$ (sp. gr. at $6^\circ = 0.7242$, smell like oranges); according to Beilstein at 150.8° . Which is right? Refined petroleum (kerosene) contains from C_9H_{20} up to $C_{16}H_{34}$, along with hydrocarbons of the formula C_nH_{2n} .

Decane, $C_{10}H_{22}$.

Syn. diamyl. Found in all tars, probably the isomer diisoamyl. Boils at $158-159^\circ$; at -30° it gets viscid; sp. gr. at $18^\circ = 0.736$. Beilstein states that the boiling-point is 161° , the sp. gr. at $16^\circ = 0.757$. O. Jacobsen* has found a decane, boiling at $170^\circ-171^\circ$, in the fractions of light coal-tar oil which pass over between 163° and 168° , along with pseudocumene and mesitylene.

Undecane, $C_{11}H_{24}$.

Found in American petroleum. Boils at $180-182^\circ$; sp. gr. at $16^\circ = 0.765$.

Duodecane, $C_{12}H_{26}$.

Syn. dicaproyl, dihexyl, laurylic hydride. Found in bog-head tar and petroleum. An oily colourless liquid, with a pleasant, turpentine-like smell, boils at $200-202^\circ$, sp. gr. at $18^\circ = 0.7568$, burns with a luminous flame, without much smoke.

* Ann. Chem. clxxxiv. p. 179.

Higher members.

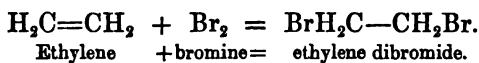
$C_{18}H_{38}$,	boiling-point	218–220°	sp. gr.	0·778
$C_{14}H_{30}$	„	236–240°	„	0·796
$C_{15}H_{32}$	„	258–262°	„	0·809
$C_{16}H_{34}$	„	about 280°		

Solid Paraffine

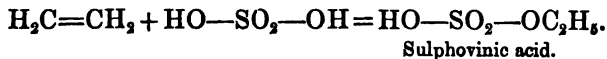
contains bodies of the formula $C_{18}H_{34}$ up to $C_{27}H_{56}$; also usually about 1 per cent. of oxygen. The paraffin found in the highest-boiling portions of real coal-tar is, according to Perkin, unlike ordinary paraffine; it fuses at a higher temperature, and is but slightly soluble in petroleum or naphtha. The proper paraffine occurs principally in tar from Scotch and Lancashire cannel coal.

HYDROCARBONS OF THE ETHYLENE SERIES, C_nH_{2n} .

The lowest members of this series are gaseous at the ordinary temperature, but occur constantly in illuminating-gas, and probably dissolved in tar. The higher ones are liquid; the highest, solid. It is characteristic of all to unite directly with chlorine, bromine, or iodine, forming oily liquids; with bromine especially the reaction is very violent. This is ascribed to the circumstance that they are non-saturated compounds (“dyad radicals”), in which carbon occurs doubly tied, so that, when one of these ties is broken, two monovalent atoms can attach themselves directly; *e.g.*



They also unite readily with the halogen hydrides HCl, HBr, and especially HI; also with hypochlorous acid, forming chlorhydrines, *e.g.* $CH_2(OH)-CH_2Cl$. Concentrated sulphuric acid absorbs them, the lower members only at higher temperatures, also by direct attachment and formation of sulpho-acids; *e.g.*



From this it follows that these compounds can be removed from the tar-oils by bromine or by concentrated sulphuric acid. In ordinary coal-tar they play but an insignificant part; but they occur copiously in cannel-coal and bog-head tar.

Ethylene, C_2H_4 .

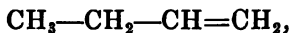
Syn. elayl. Liquefies at 0° only under a pressure of $42\frac{1}{2}$ atmospheres, at -110° under the ordinary pressure. Sp. gr. 0.9784. Water at 0° dissolves 0.25 vol., at 15° 0.16 vol. Much more dissolves in alcohol, ether, oil of turpentine, petroleum (about $2\frac{1}{2}$ vols.), hence probably also in tar-oils. Concentrated sulphuric acid absorbs it on prolonged agitation, better at 160 – 175° C., fuming oil of vitriol much more quickly, with formation of ethionic acid.

Propylene, C_3H_6 .

Syn. tritylene. Not yet liquid at -140° , possessing an alliacious smell. 100 vols. of water dissolve at 0° 44 vols., at 15° 23 vols.; absolute alcohol 12–15 vols., glacial acetic acid 5 vols. Its chemical behaviour is like that of ethylene.

Butylene, C_4H_8 .

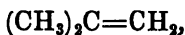
Syn. tetrylene, ditetryl. Three isomers are possible and known. First condensed by Faraday from the lighting-gas obtained from fatty oils, by strong pressure. Normal butylene,



boils at -5° ; pseudobutylene,



at $+1^\circ$; isobutylene,



at -7° or -8° .

Amylene, C_6H_{10} .

Syn. pentylene, valerene. Of the five possible isomers, only that is well known which is obtained from amylic alcohol by water-abstracting reagents, especially zinc chloride. Whether this is identical with the amylene found in coal-tar* and much more abundantly in bog-head tar, petroleum, &c., or not, is not quite certain; but this is usually assumed to be the case. At all events several amylenes occur in tar, probably also polymers.

* Helbing, Ann. der Chem. clxxii. p. 281. Watson Smith (priv. comm.) has also found amylene in the first runnings of London tar, along with carbon bisulphide.

. Ordinary amylene is a limpid, mobile liquid, of cooling, astringent, and somewhat pungent taste, and smelling somewhat like rotten cabbages. Its boiling-point is variously stated at from 33° to 42° (that obtained from amylic alcohol boils at 39°). Sp. gr. at $10^{\circ}=0.6549$. It is but sparingly soluble in water, but indefinitely miscible with alcohol. Like its congeners it unites directly with Cl, Br, HCl, HBr, HI, also with NO_2 and HOCl. Oxidizing substances (potassium permanganate, chromic acid, &c.) convert it into fatty acids, carbon dioxide, ketones, &c. With sulphuric acid, Berthelot says*, it yields an acid isomer to sulphamylic acid, which Erlenmeyer† could not find. However this may be, all the isomers dissolve in sulphuric acid at ordinary temperatures, some of them even when it is not fully concentrated.

Amylene was used for some time as an anæsthetic, in lieu of chloroform.

Hexylene, C_6H_{12} .

Syn. caproylene. Of the many isomers, tar seems to contain essentially the normal, the only one pretty well known; but other isomers are probably present as well. Normal hexylene is a colourless, mobile liquid, smelling like amylene, boils at $68-70^{\circ}$; sp. gr. at $0^{\circ}=0.6996$; insoluble in water, readily soluble in ether and alcohol; chemically quite analogous to amylene. Sulphuric acid, diluted with $\frac{1}{3}$ vol. water, dissolves in the cold its volume of hexylene, from which mixture secondary hexylic alcohol soon separates. Concentrated sulphuric acid colours it reddish brown, gives off SO_2 , and turns it into a thick oil.

Heptylene, C_7H_{14} .

Syn. cœnanthylene. Like the above, found in bog-head tar. A limpid, mobile liquid with an alliaceous smell. Boils at 94° (Pelouze and Cahours), 96° (Schorlemmer), 99° (C. G. Williams). Sp. gr. at $18^{\circ}=0.718$ (C. G. Williams), at $17^{\circ}.5=0.7383$ (Schorlemmer). Its chemical behaviour is like that of the two foregoing compounds.

AROMATIC ADDITION-PRODUCTS, C_nH_{2n} .

According to Beilstein and Kurbatow‡, the hydrocarbons of Caucasian petroleum having the formula C_nH_{2n} are not identical

* Compt. Rend. lvi. p. 1242.

† Zeitschr. f. Chemie, 1865, p. 362.

‡ Ber. deutsch. chem. Ges. 1880, pp. 1818, 2028.

with the compounds of the preceding series; such occur also in American petroleum along with heptane &c. They were found identical with the hydrogen-addition products of aromatic hydrocarbons discovered by Wreden*, viz. :—

		Sp. gr. at 0°.	Boils at
Hexahydrobenzene.....	C_6H_{12}	0·76	69° C.
Hexahydrotoluene	C_7H_{14}	0·772	97
Hexahydroisoxylene	C_8H_{16}	0·777	118

Schützenberger and Ionine†, who confirm the above, propose the name *paraffenes* for these compounds, inactive towards bromine, sulphuric acid, and nitric acid.

HYDROCARBONS OF THE ACETYLENE SERIES, C_nH_{2n-2} .

Acetylene itself, C_2H_2 , is a gas, and can only be dissolved in very small quantity in tar. Schorlemmer ‡ has found in the light oil from cannel coal, after treatment with sulphuric acid, polymers of the acetylene series having the general formula $(C_nH_{2n-2})_x$, viz. :—

$C_{12}H_{20}$,	boiling at 210° C.
$C_{14}H_{24}$	„ 240
$C_{16}H_{28}$	„ 280

They are colourless oily liquids, lighter than water, smelling like carrots or *Pastinaca sativa*. They unite directly with bromine, with a violent reaction; in concentrated nitric acid they dissolve; and on diluting the solution with water, oily nitro-compounds separate. Since the original oils boiled below 120°, they cannot have contained these bodies, but those of the acetylene series, C_nH_{2n-2} , itself. In coal-tar they probably play even a less important part than in cannel-tar. But to acetylene itself a very important function in the formation of aromatic hydrocarbons is ascribed (see below).

Crotonylene, C_4H_6 .

Discovered in 1863 by Caventou; since then prepared synthetically and found in coal-tar§. A colourless liquid, boiling at 18°. Probably ethyl-acetylene, $C_2H_5 \cdot C \equiv CH$.

* Liebig's Annalen, clxxxvii. p. 166.

† Compt. Rend. xci. p. 828.

‡ Chem. News, xiii. p. 253.

§ Caventou, Bull. Soc. Chim. [2] xix. p. 245; Helbling, Ann. der Chemie, clxxii. p. 281.

Hexylene, C_6H_{10} .

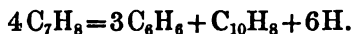
Syn. diallyl. A colourless liquid, with a penetrating alliaceous smell, boiling at $76-80^\circ$; sp. gr. at $13^\circ = 0.71$.

HYDROCARBONS OF THE SERIES C_nH_{2n-4} .

One such, *nonene*, C_9H_{14} , the next lower homologue of oil of turpentine, has been found by Tawildarow* in tar, viz. in the portion distilling after cumene, between 175° and 190° . On fractionating, most came over at 174° . This body does not appear to have been obtained in a pure state; and its existence cannot be considered completely established.

HYDROCARBONS OF THE BENZENE SERIES, C_nH_{2n-6} .

We have seen above (pp. 3 and 9) that the compounds of this series, which commence the large class of the so-called aromatic compounds, are specifically characteristic of coal-tar. They occur also in the tar from wood, browncoal, shale, &c., but therein occupy a subordinate position. But they are also formed by many reactions, above all by the action of heat, partly from their own higher homologues or other derivatives, partly by the decomposition or by the molecular condensation of fatty compounds. By the action of high temperatures, *e.g.* by passing the vapour through red-hot tubes, benzene is formed not merely from toluene, xylene, styrolene, &c., but also from alcohol, acetic acid, ethylene, methane, frequently along with naphthalene; *e.g.*



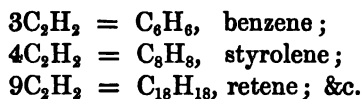
Of course, even more highly condensed molecules, such as anthracene, phenanthrene, chrysene, &c., in a similar way are formed, hydrogen being eliminated. By passing the mixed vapours of benzene and toluene through red-hot tubes Carnelley† obtained naphthalene, diphenyl, paratolylphenyl, orthoparadiphenyl, two methylene diphenylenes, phenanthrene, anthracene, paradiphenylbenzene, a hydrocarbon $C_{32}H_{28}$, a liquid hydrocarbon fusing at 13° and boiling at $290-316^\circ$, two other liquid hydrocarbons (or mixtures of hydrocarbons) boiling at $359-383^\circ$ and $404-427^\circ$, and solid black bitumen.

* Zeitsch. f. Chemie (2), 1868, iv. p. 278.

† Journ. Chem. Soc. Nov. 1880, p. 701.

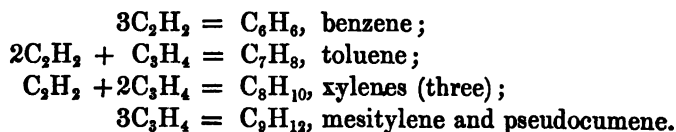
It thus becomes conceivable why (as stated on p. 8) destructive distillation at lower temperatures yields more of fatty bodies and less of permanent gases, at higher temperatures more of aromatic compounds and more of permanent gases, and why, by passing the heavy hydrocarbons of the fatty class (from wood-tar, shale-tar, petroleum, &c.) through red-hot tubes, benzene and its derivatives can be prepared on a large scale (p. 22).

One of the most important parts in the formation of these bodies seems to be played by acetylene. According to Berthelot*, on heating acetylene over mercury in a bent tube up to the softening-point (*i. e.* to a dark red) there was produced, along with a number of secondary products occurring in small quantity, a large amount of benzene, styrolene, naphthalene, retene, &c. At a bright red heat another kind of decomposition set in; then acetylene was almost completely split up into its elements. Berthelot consequently views benzene as triacetylene, styrolene as tetracetylene, retene as enneacetylene: thus,



The fatty bodies likewise yield acetylene under the action of heat; and Berthelot ascribes the formation of aromatic compounds, always observed in this case, to the secondary condensation of acetylene by itself and with other compounds.

Similar conclusions are arrived at by O. Jacobsen†, who, besides acetylene, assumes its next homologue, allylene, C_3H_4 , to participate in the synthesis. This is shown by these equations:



This hypothesis would explain why,

1st, besides benzene, only those homologues occur whose lateral chains consist of methyl;

2nd, the methylbenzenes found in tar-oil do not extend beyond the tri-derivatives;

* Compt. Rend. lxii. pp. 905, 947.

† Ber. deutsche chem. Ges. 1877, p. 853.

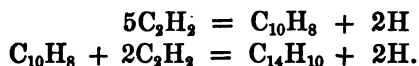
3rd, of all possible tri-derivatives only mesitylene and pseudo-cumene are present ;

4th, all three xylenes occur in tar-oil.

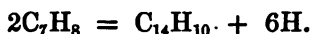
(The last is made clear by the graphic reaction schemes given in the original.)

Allylene has not yet been observed among the products of destructive distillation ; but Jacobsen ascribes this to its easier condensation, and to the difficulty of discovering small quantities of it mixed with acetylene.

Even on Jacobsen's theory the formation of the other hydrocarbons occurring in tar can only be explained by elimination of hydrogen, as shown by Anschütz*:



Anthracene and phenanthrene might also be formed by a condensation of ditoluene :



It is an argument in favour of Jacobsen's theory, that tar has certainly been found to contain only methylated benzene homologues, exactly those mentioned by him, but neither cumene (isopropylbenzene), nor propylbenzene, nor ethylmethylbenzene. It is true that older treatises enumerate cymene (methyl-isopropylbenzene) as a constituent of tar, but upon insufficient evidence ; so that nowadays cymene is not considered to be present in tar.

Benzene, C₆H₆.

Syn. benzol (this word is now mostly used for the commercial mixture of benzene, toluene, &c. in varying quantity), phenylic hydride. It was discovered in 1825, by Faraday, in the liquid separating from condensed oil-gas. Mitscherlich in 1833 prepared it by the dry distillation of calcium benzoate, determined its empirical formula, and conferred upon it its present name ; he also discovered nitrobenzene. Its first discovery in coal-tar is claimed by Leigh, who states that his communication to that effect was made to the British Association meeting in 1842, but omitted to be mentioned in its Report by an oversight†. At all events

* Ber. deutsch. chem. Ges. 1878, p. 1215.

† Moniteur Scientif. 1865, p. 446.

that observation remained unknown and sterile; and the credit of having, in 1845, distinctly recognized the presence of benzene in coal-tar, and proved it by transforming it into nitrobenzene and aniline, will not be denied to A. W. Hofmann*. The process for obtaining it in any quantity from coal-tar was worked out in his laboratory by one of his pupils, Charles Mansfield†, who carried out the process on the large scale and minutely described the principle of dephlegmation for separating the various hydrocarbons; he distinctly pointed out that the apparatus employed in rectifying spirit might be employed for this purpose, even with greater advantage than for spirit of wine itself‡—a suggestion usually, but erroneously, stated to be due to E. Kopp, who first speaks of it in 1860§. Mansfield already utilized the property possessed by benzene (observed first by Faraday), of crystallizing at 0°, for preparing it in a state of perfect purity. It is allowed to freeze in a freezing-mixture; the liquid portion is pressed out; and, if necessary, the operation is repeated. Hofmann|| has shown that the crystals easily enclose mother-liquor, which causes the product to contain toluene. Hence he prescribes preventing the formation of large crystals and completely separating the mother-liquor by atmospheric pressure, for which purpose he describes a convenient laboratory-apparatus.

Benzene is formed, on the one hand, by synthesis (condensation) from acetylene and other fatty compounds of simpler molecular constitution, and, on the other, by the splitting-up of more complex compounds, both fatty and aromatic, in both cases by the action of strong heat. In sealed tubes it remains unchanged even when heated to 400° C. Hence it is one of the most stable organic compounds; but on passing through red-hot tubes it also is decomposed, more highly condensed hydrocarbons, especially diphenyl, being formed (Berthelot, Schulze¶, Schmidt**, Behr und von Dorp††). Passed through red-hot tubes along with ethylene, it yields styrolene, naphthalene, diphenyl, acenaphthene, anthra-

* Ann. Chem. Pharm. liv. p. 204.

† Engl. Patent No. 11,960, of Nov. 11, 1847; Q. J. Chem. Soc. i. p. 244.

‡ Lecture at the Royal Institution, April 27, 1849.

§ Moniteur Scientif. 1860, vol. ii. p. 829.

|| Ber. deutsch. chem. Ges. 1871, p. 162.

¶ Ann. Chem. clxxiv. p. 201.

** Ber. deutsch. chem. Ges. 1874, p. 1365.

†† Ibid. 1873, p. 723.

cene, &c. (Berthelot), all of which must consequently be found in crude illuminating-gas and the tar therefrom.

Benzene is a colourless mobile liquid of peculiar smell. Its boiling-point is stated at 80–81° (Mansfield), 80°·4 at a pressure of 760 millim. (Kopp), 80°·1 (Warren), 80°·36 (Regnault). Adrieenz* found that benzene prepared from tar boils at 80°·53–80°·62, that from benzoic acid at 80°·60–80°·67. The temperature of a boiling mixture of benzene and water is 68°·5, that of the vapour 69°·1†. At 0° it solidifies to a mass of crystals, which fuse at 4°·45 (Regnault) or 7° (Mitscherlich). The crystals are orthorhombic prisms, whose axes $a : b : c$ have the ratio 0·891 : 1 : 0·799‡. Its specific gravity at 0° = 0·8991 (Kopp), at 15° = 0·884 (Mendeleeff); at 0° = 0·8957, at 15° = 0·8820 (Warren). Its coefficient of expansion is stated by Kopp for the temperature t (between 11°·4 and 81°·4) to be

$$V_t = 1 + 0\cdot001171626t + 0\cdot00000127755t^2 + 0\cdot0000000080648t^3.$$

Adrieenz gives the following table for the specific gravity of benzene (from benzoic acid) :—

Temp.	Sp. gr.	Volume.	Temp.	Sp. gr.	Volume.
0	0·90023	1	45	0·85291	1·05550
5	0·89502	1·00582	50	0·84748	1·06228
10	0·88982	1·01169	55	0·84198	1·06924
15	0·88462	1·01764	60	0·83642	1·07637
20	0·87940	1·02367	65	0·83078	1·08370
25	0·87417	1·02979	70	0·82505	1·09123
30	0·86891	1·03603	75	0·81923	1·09898
35	0·86362	1·04238	80	0·81331	1·10696
40	0·85829	1·04887			

The specific gravity of benzene from tar-oil he found at 0° = 0·90122 and 0·90129.

The specific heat of benzene between 19° and 46° = 0·450 (Kopp). Its refraction-index§ for the line A is 1·4593; for D it is 1·5050; and for H, 1·5307; Adrieenz gives 1·4957 at 15°·2 for D.

Benzene is not merely a most important substance for industrial

* Ber. deutsch. chem. Ges. 1873, p. 441.

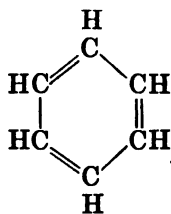
† Naumann, Ber. deutsch. chem. Ges. 1877, p. 142.

‡ Groth, Pogg. Ann. cxli. p. 31.

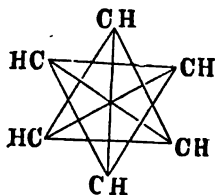
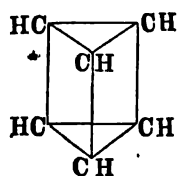
§ Gladstone, Chem. Soc. Journ. 1870, vol. xxiii. p. 152.

purposes, but even more so for theoretical chemistry. The enormous array of aromatic compounds are all derived from benzene. It would seem well-nigh impossible to find one's way through this interminable field, if Kekulé's celebrated theory of the constitution of benzene had not brought light and order into it. It can be stated without fear of contradiction, that without Kekulé's hexagon formula nothing like so many and so important aromatic compounds would have been discovered as there have been; his hypothesis is certainly one of the most fertile and suggestive that have ever been propounded in chemistry.

Nearly all chemists agree with Kekulé in assuming that the six carbon atoms of benzene are united in a closed chain (nucleus), and that, of the four bonds of each atom, three are satisfied by other carbon atoms of the same nucleus, the fourth being satisfied by hydrogen atoms. But opinions differ on the special kind of bond. According to Kekulé's hypothesis, each carbon atom is chained with one bond to one and with two bonds to another of its neighbours, as expressed by the graphic formula



A more modern formula, first mentioned by Claus, then adopted by Ladenburg, pictures each carbon atom connected by three single bonds with three other atoms—which can be graphically represented either by a prism or a star,



Many reasons support the latter formula, as well as the combustion-heat of benzene*; hence it has now been adopted by

* Thomson, Ber. deutsch. chem. Ges. 1880, p. 1808.

many chemists. But, for the sake of simplicity, benzene is usually represented merely by the figure of a hexagon, and its derivatives by attaching the respective groups to the corners, whilst the empty corners are understood to be filled with hydrogen atoms.

Benzene is very little soluble in water, but sufficiently so to communicate its smell. It is easily soluble in alcohol, ether, wood-spirit, acetone, &c. It dissolves iodine, sulphur*, phosphorus (when hot), and (very easily) fats, ethereal oils, resins, &c. It is easily inflammable, as well as its vapour, which necessitates great precaution in storing it in quantity. It burns with a strongly smoking flame. Ordinary gas passed through benzene gains very much in illuminating-power; Berthelot even ascribes that of (Paris) lighting-gas essentially to the benzene contained in it, whilst formerly substances of the ethylene series received the credit. This has been confirmed by the researches of Knoblauch†, and is now pretty generally assumed to be correct. Even atmospheric air passed through benzene yields a mixture burning with a bright flame, upon which property Mansfield at that time (before the discovery of the aniline colours) founded his hopes of an industrial utilization of benzene. Frankland and Thorne‡ have made a quantitative investigation of the illuminating-power of benzene when mixed in the state of vapour with non-luminous gases.

The changes undergone by benzene when passed through red-hot tubes have been mentioned above (p. 35).

Concentrated sulphuric acid at ordinary temperature acts very little upon benzene, for which reason the latter can be purified by treatment with that acid. But on heating benzene-monosulphuric acid ($C_6H_5 \cdot SO_3H$) is formed, and at very high temperatures, or more easily by fuming sulphuric acid, benzene-disulphuric acid ($C_6H_4(SO_3H)_2$). Concentrated nitric acid converts benzene into nitro-compounds (mono- and dinitrobenzene), upon which its detection, its estimation, and, to a great extent, its industrial application are based. Oxidizing reagents, such as potassium permanganate, manganese dioxide, chromic acid, &c., act upon it

* The somewhat considerable solubility of sulphur in benzene and ether (also the heavy tar-oils) has been studied in detail by E. Pelouze, junior (Compt. Rend. lxxviii. p. 1179, lxxix. p. 56).

† Ber. deutsch. chem. Ges. 1881, p. 240.

‡ Chem. News, xxxvii. pp. 36, 72.

but little and with formation of complex products. Chlorine and bromine yield with it addition and substitution products.

Toluene, $C_7H_8 = C_6H_5 \cdot CH_3$.

Syn. methylbenzene. It was discovered in 1838, by Pelletier and Walter, in the condensation-products from the manufacture of rosin-gas, and was called "retinaphtha." Afterwards Deville obtained it by destructive distillation of tolu balsam; the name of toluene (toluol) was given to it by Berzelius. Mansfield found it in coal-tar; and it has since been met with in many mineral oils. Its formation, together with that of analogous compounds, has been mentioned above. It is obtained from coal-tar in very large quantities, and if necessary in a state of comparative purity, and is largely employed, partly for the manufacture of colouring-matters, partly as a solvent. It is much more difficult to prepare in a perfectly pure state than benzene, because it does not crystallize.

The received theory admits only one toluene; and in fact it has been proved by Berthelot* and Rosenstiehl† that all toluenes, whatever may be their origin, are identical.

Toluene is a colourless, mobile, strongly refractive liquid. Its boiling-point is 110° (Wilson), or 111° (Wilbrand and Beilstein), or $110^\circ.3$ (Warren). It does not solidify at -20° . Its specific gravity at $0^\circ = 0.8824$, at $15^\circ = 0.8720$ (Warren); or at $0^\circ = 0.8841$, at $15^\circ = 0.8702$ (Louguinine). The latter states its volume at the temperature t , if at $0^\circ = 1$, as

$$V_t = 1 + 0.001028t + 0.000001779t^2.$$

Deville gives 1.4899 as its refraction-index.

The smell of toluene is rather different from that of benzene. It is insoluble in water, but communicates its smell to it; it is miscible with alcohol, ether, carbon bisulphide, &c. It dissolves sulphur, phosphorus, iodine, fats, &c. When ignited, it burns with a bright and strongly smoking flame. Passed through red-hot tubes it yields benzene, naphthalene, anthracene, phenanthrene, &c.

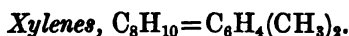
According to Berthelot, toluene possesses, similarly to oil of turpentine, the property of rendering oxygen active; when toluene

* Bull. Soc. Chim. 1869, xi. p. 381.

† Ibid. xi. p. 385.

is shaken up with a very dilute tepid solution of indigo in the presence of air, decolorization takes place.

Concentrated sulphuric acid dissolves toluene on heating and prolonged shaking; fuming acid does so much more quickly. In this two isomeric sulphacids are formed. Nitric acid of less than 1.42 sp. gr. does not act upon it when cold; but fuming nitric acid does so violently, even more so than upon benzene, nitro-products up to trinitrotoluene being formed. Oxidizing agents (dilute nitric acid, chromic acid, potassium permanganate) convert it into benzoic acid, but only with difficulty and great loss, so that this direct oxidation is scarcely practised on an industrial scale.



Syn. dimethylbenzene. Xylene (*i. e.* a mixture of the isomers) was discovered in 1850, by Cahours, in crude wood-naphtha. In coal-tar it was found by Ritthausen and Church. Latterly it has been synthetically produced by Friedel and Crafts, by treating benzene or toluene with methylic chloride in the presence of aluminium chloride.

The xylene of coal-tar, even when entirely freed from its homologues, still showed great differences in the hands of different observers. In the purest state it boils at 138–140°; and at 0° its sp. gr. is = 0.877. Its volume between 0° and 100° is expressed, according to Louguinine, by the formula

$$V_t = 1 + 0.0009506t + 0.000001632t^2.$$

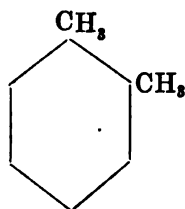
Steam passed into xylene carries it along. The mixed vapour has a temperature of 91.5°, and contains, for 100 parts of xylene, 44 of water, independently of the shape of the vessel and the speed of distillation (Naumann*).

Fittig first proved in 1869† that coal-tar xylene is not a homogeneous body; he stated it to contain 90 per cent. metaxylene and 10 paraxylene. But O. Jacobsen‡ has proved the presence of orthoxylene, and estimates the proportion at 70–75 per cent. metaxylene, 20–25 paraxylene, and 10–15 orthoxylene; in any case different tars will differ in this respect.

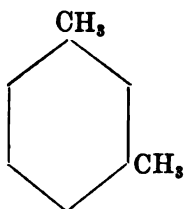
* Ber. deutsch. chem. Ges. 1877, p. 1426.

† Ann. der Chemie, cliii. p. 265.

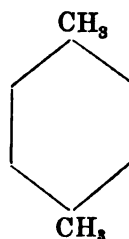
‡ Ber. deutsch. chem. Ges. 1877, p. 1009.



Orthoxylene.



Metaxylene.



Paraxylene.

Orthoxylene is a colourless liquid, whose pleasant aromatic smell differs from that of its isomers. It boils at $141-143^{\circ}$, and is not yet solid at -22° . It dissolves in concentrated sulphuric acid.

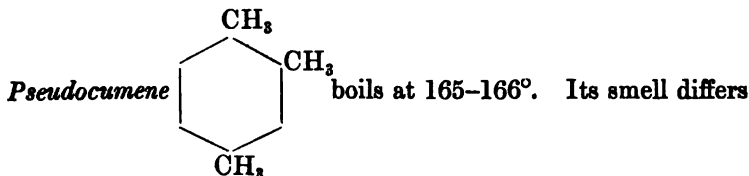
Metaxylene (*syn.* isoxylene) boils at $137-138^{\circ}$, is also soluble in concentrated sulphuric acid; forms the principal part of the mixture of xylenes in coal-tar.

Paraxylene fuses at 15° , and boils at $136-137^{\circ}$. Like the preceding, it has a peculiar smell, different from that of benzene. According to Glinzer and Fittig, its sp. gr. (not quite pure) at $18^{\circ}5 = 0.8625$. It is very little acted upon even by hot concentrated sulphuric acid; but faintly fuming oil of vitriol dissolves it, forming a sulpho-acid which can be precipitated by water and purified by recrystallization, and from which by dry distillation pure paraxylene is regenerated. This behaviour shows how it can be isolated. The tar isomers dissolved in sulphuric acid can be separated in the following way (Jacobsen). As much as possible of the excess of sulphuric acid is removed by calcium carbonate; the liquid is mixed with a slight excess of sodium carbonate, and the filtrate evaporated so far that on cooling a considerable crop of salt is obtained. This sodium orthoxylene-sulphonate can be purified by recrystallization, whilst the mother liquors contain sodium metaxylene-sulphonate. From these salts the hydrocarbons are obtained by dry distillation or by heating with hydrochloric acid to 195° . Besides, coal-tar xylene contains a body similar to paraffine, insoluble even in fuming oil of vitriol, which is not yet examined.

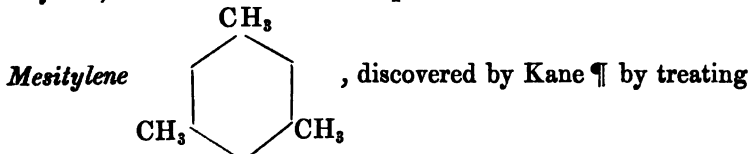
Probably in coal-tar itself orthoxylene occurs in much larger quantity than has been found by Jacobsen in commercial crude xylene. The latter has been obtained in the rectification of tar-oils previously treated with concentrated sulphuric acid, which must have dissolved much orthoxylene.

Trimethylbenzenes, $C_9H_{12} = C_6H_3(CH_3)_3$.

Already Mansfield found hydrocarbons of the empirical formula C_9H_{12} in coal-tar, but evidently not in the pure state. Like him the other chemists for a number of years believed they had to do with a homogeneous body, identical with the retinyl obtained in 1837 by Pelletier and Walter from rosin-oil, or cumene (cumol, propylbenzene), obtained by Gerhardt and Cahours from cuminic acid. Often even xylene was confounded with cumene. This was cleared up by Beilstein*, who described the substance, freed from homologues, as *pseudocumene*. Already Warren† had obtained it in a similar state, boiling at $169^{\circ}8$. But Fittig and his disciples‡ proved that Beilstein's pseudocumene is a mixture of two isomeric trimethylbenzenes, viz. that of pseudocumene, in the present sense of the term (1, 2, 4), and of mesitylene (1, 3, 5). Besides them O. Jacobsen§ has found a paraffine, $C_{10}H_{22}$, boiling at 170 – 171° . The same chemist has described || the preparation of both hydrocarbons in a pure state; but this is a most roundabout process, quite unsuited for industrial use.



from that of the lower homologues. It is insoluble in water, soluble in ether and alcohol, but only little soluble in glacial acetic acid (like mesitylene). Treated with sulphuric acid it dissolves (like mesitylene) with formation of a sulpho-acid.



acetone with sulphuric acid, by Fittig in coal-tar oil. Boils at 163° (Fittig); smells rather like garlic.

ADDITION-PRODUCTS of the benzene series have been mentioned on p. 33.

* Ann. Chem. Pharm. cxxxiii. p. 32.

† Chem. News, xii. p. 292.

‡ Ann. Chem. Pharm. cxxxix. p. 184; cxlv. p. 137; cl. pp. 257, 283, 292.

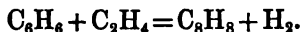
§ Ann. d. Chemie, clxxxiv. p. 179.

|| Ber. deutsch. chem. Ges. 1876, p. 256.

¶ Poggend. Ann. xlv. p. 474.

Styrolene, $C_8H_8 = C_6H_5 \cdot CH=CH_2$.

Syn. cinnamene, phenylethylene. Usually obtained from storax or Peru balsam; synthetically by Berthelot* by condensation of acetylene at the temperature of softening glass, or, better, by passing a mixture of benzene and acetylene through red-hot, and even better through white-hot tubes, thus:

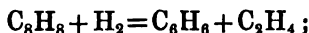


These reactions explain the occurrence of styrolene in coal-tar, in which, however, it occurs only in insignificant quantities.

It is a colourless mobile oil, with a strong aromatic smell, reminding one of benzene and naphthalene. It does not solidify at -20° , boils at 145° , but volatilizes at ordinary temperature, so that it does not leave a grease-spot on paper. Sp. gr. at $16^\circ = 0.876$. Its solubilities are quite analogous to those of benzene. Caustic potash has no action upon it; fuming sulphuric acid converts it into a sulpho-acid, ordinary sulphuric acid only into a solid polymer, which, on distillation, is reconverted into styrolene. Chlorine and bromine unite directly with it. Fuming sulphuric acid dissolves it, forming a nitro-compound. At a red heat it splits up into benzene and acetylene,



or, if mixed with hydrogen, into benzene and ethylene,



that is, the reaction is the inverse of that which took place in its formation. Heated with ethylene it yields benzene and naphthalene; heated with benzene, naphthalene and anthracene. It probably plays an important part in the formation of these higher hydrocarbons, and, for that very reason, does not occur in large quantities in coal-tar.

Styrolene hydride, C_8H_{10} .

?

Naphthalene, $C_{10}H_8$.

Discovered by Garden in 1820; first studied in detail by Laurent. It is formed in innumerable cases by the action of heat

* Compt. Rend. lxiii. p. 481, 518, 702, 834; lxviii. p. 327.

on organic substances, but only at rather high temperatures; so that tar obtained at a comparatively low heat does not contain it at all. In gas-tar it always occurs, but in very varying quantities, very much greater since the cast-iron retorts have been replaced by fireclay retorts worked at much higher temperatures. The statement of Calvert *, that Newcastle tar contains 58 per cent. of naphthalene, is absurd on the face of it; ordinarily tar rarely contains more than from 5 to 10 per cent. The mode of its formation has been explained on pp. 35 and 37.

In the pure state it forms white crystalline masses, or thin rhomboidal scales; on spontaneous evaporation of an ethereal solution it appears in monoclinic prisms (Laurent). It fuses at 79° ; the statements respecting its boiling-point vary between 212° and 220° ; but 217° seems to be the correct figure. Sp. gr. at $18^{\circ}=1.158$, at $79^{\circ}.2=0.9778$. Melted naphthalene, according to Vohl †, absorbs a large quantity of air, which is given off again on cooling; it is said to be much richer in oxygen than atmospheric air. Naphthalene volatilizes far below its boiling-point, and distils both with aqueous vapour and with that of light tar-oils; hence it always appears with the latter in crude tar-oils. Even at ordinary temperature it volatilizes slowly and gives off a penetrating tarry smell, which clings a long time to clothes &c., and is said to keep off moths and other vermin. Ballo ‡ asserts that this smell is not that of pure naphthalene, but of leucolin oil; however, the purest obtainable naphthalene exhales it quite strongly. Its taste is pungent. It burns with a strongly smoking flame; but its vapour mixed in small quantity with gas considerably enhances the illuminating-power of the latter.

It is insoluble in cold § but not quite so in hot water; so that the latter turns milky on cooling. It is easily soluble in alcohol, ether, fatty and essential oils, and acetic acid, very much so in phenols, but less easily in the indifferent tar-oils. When melted it dissolves phosphorus, sulphur, indigo, and several metallic sulphides, which crystallize on cooling. According to Bechi ||, 100 parts of absolute alcohol at 15° dissolve 5.29 parts, at the boiling-

* Compt. Rend. xlix. p. 262.

† Journ. f. prakt. Chem. cii. p. 29.

‡ Dingler's Journ. ccii. p. 377.

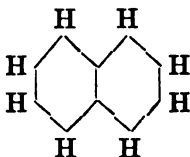
§ Lupton (Chem. News, xxxiii. p. 90) doubts this, but does not adduce any positive proof to the contrary.

|| Ber. deutsch. chem. Ges. 1879, p. 1928.

point any quantity; 100 parts of toluene at $16^{\circ}5$ 31.94 parts, at 100° any quantity.

Alkalies do not act upon naphthalene. Concentrated sulphuric acid, on heating, converts it into sulpho-acids—below 70° principally into the α , at 160° almost entirely into the β modification. This behaviour is very important, because the corresponding naphthols can only be made from the proper sulpho-acids. Chlorine yields both addition and substitution products; nitric acid, nitronaphthalene.

The constitution of naphthalene has been elucidated chiefly by the researches of Erlenmeyer* and Graebe†; it is generally assumed to consist of two benzene nuclei, attached to each other by two carbon atoms, thus—



In order to prove the presence of naphthalene, Vohl treats the substance in question with fuming nitric acid, adds a large quantity of water, washes the precipitated nitro-compound, and puts it into a boiling mixture of 1 part potassium monosulphide and 1 part caustic potash; traces of naphthalene yield a beautiful purple solution.

Naphthalene dihydride, $C_{10}H_{10}$.

Discovered by Berthelot‡ as a product of the action of concentrated hydriodic acid on naphthalene; occurs also in coal-tar. A viscid fluid, with a strong, disagreeable smell, boiling at 200 – 210° . Is powerfully acted upon by bromine, and dissolves in cold fuming nitric acid.

Naphthalene tetrahydride, $C_{10}H_{12}$.

Occurs in small quantity along with the dihydride; it boils at 190° . Its other properties are similar to those of the latter body.

β . *Methylnaphthalene*.

Reingruber§ found this in that portion of coal-tar which distils

* Ann. Chem. Pharm. cxxxvii. p. 346.

† Zeitschr. f. Chemie (2), iv. p. 114.

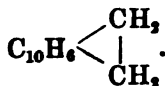
‡ Bull. Soc. Chim. 1868, ix. p. 287.

§ Ann. Chem. ccvi. p. 367.

between 220° and 270°, and which remains liquid at ordinary temperature. It is a colourless oil, with blue fluorescence and a faint, not disagreeable smell, boiling at 242–243°, and crystallizing at –18–20° to a hard mass. It is miscible in all proportions with absolute alcohol, ether, benzene, carbon bisulphide, and glacial acetic acid. Oxidizing agents act briskly upon it, and destroy it with evolution of carbon dioxide.

Acenaphthene, $C_{12}H_{10}$.

Occurs in that portion of coal-tar which boils at 270–300°, especially between 280° and 290°, and crystallizes on cooling. By recrystallizing from light tar-oil or alcohol, or cautious subliming, it is obtained pure*. It fuses a little above 100°, solidifies at 95°, and boils at 285°. Crystallized from alcohol it forms long, colourless, shining needles; from heavy tar-oils it separates in hard, brittle crystals. Its smell resembles that of naphthalene. It is little soluble in cold, easily in boiling alcohol. Bromine acts readily upon it; concentrated sulphuric acid dissolves it, forming a sulphonic acid, of which all the salts are easily soluble; concentrated nitric acid forms a nitro-compound. Its constitution is

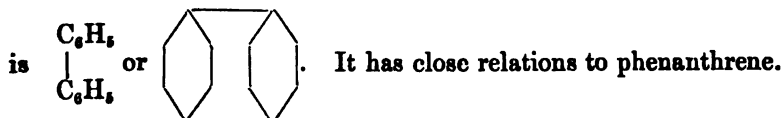


Acenaphthene hydride, $C_{12}H_{12}$.

Is stated by Berthelot to occur along with the preceding body in coal-tar. It boils at 260°.

Diphenyl, $C_{12}H_{10}$.

Discovered in 1862 by Fittig†. It occurs in that fraction of coal-tar which boils at from 220° to 270°‡. It fuses at 70°·5, and boils at 254°. It readily dissolves in alcohol and ether, and crystallizes in large colourless scales. Bromine, sulphuric acid, nitric acid act upon it, and form corresponding derivatives. Its rational formula



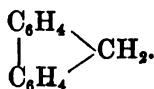
* Berthelot, Ann. Chim. Phys. (4) xii. p. 226.

† Ann. Chem. Pharm. cxxi. p. 361.

‡ Fittig and Büchner, Ber. deutsch. chem. Ges. 1875, p. 22.

Fluorene, $C_{13}H_{10}$.

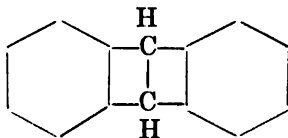
Syn. diphenylene methane. Prepared by Berthelot* from coal-tar, synthetically by Graebe, Fittig, and others in various ways; exactly examined by Barbier†. It is obtained from the fraction of coal-tar boiling between 290° and 350° , after naphthalene and anthracene are separated by fractional distillation; the portion distilling between 295° and 310° is purified by repeated recrystallization from alcohol. It forms colourless scaly crystals with a violet fluorescence, little soluble in cold, easily in hot alcohol, also in ether, benzene, carbon bisulphide. Fuses at 113° , boils at 295° , but volatilizes with aqueous vapours. Bromine and nitric acid yield derivatives with it. The rational formula is



There is a series of isomers of this formula ‡ which are probably partly contained in coal-tar.

Anthracene, $C_{14}H_{10}$.

Discovered by Dumas and Laurent in 1832, and described as *paranaphthalene*; more exactly examined in 1857 by Fritzsche, who was the first to find it in coal-tar. This was confirmed by Anderson's extended investigation in 1862. Synthetically it was first prepared by Limpricht § in 1866, from benzylic chloride, in the same year by Berthelot, pyrogenetically, from simpler hydrocarbons. The most momentous epoch in its history was marked by Graebe and Liebermann's discovery, in 1868, that it is formed from alizarine by the reducing action of zinc dust, and that alizarine can be synthesized from it. The same chemists established the structural formula of anthracene, but first gave it that now generally ascribed to phenanthrene. Anthracene is now universally represented thus,



* Compt. Rend. lxx. p. 465.

† Compt. Rend. lxxvii. p. 442; lxxix. p. 1151.

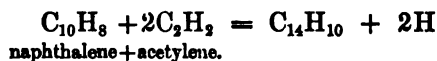
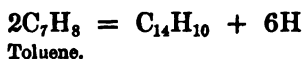
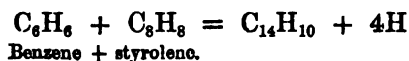
‡ Carnelly, Journ. Chem. Soc. Nov. 1880, p. 701; Lunge and Steinkauler Ber. deutsch. chem. Ges. 1880, p. 1656.

§ Ann. Chem. Pharm. cxxxix. p. 308.

or, simpler, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH} \\ | \\ \text{CH} \diagdown \end{array} \text{C}_6\text{H}_4$, *i. e.* two benzene nuclei, con-

nected by two carbon atoms which are united with each other by another bond. It is also now ascertained that both bonds are in the ortho-position towards the benzene nuclei.

The mode of its formation from other hydrocarbons appears from the following equations :—



&c. &c.

Its preparation from the highest-boiling constituents of coal-tar, and the analysis of crude anthracene, will be minutely described in Chapter VI. The preparation of chemically pure anthracene (which is not a commercial article) is not easy, unless crude anthracene distilled over caustic potash can be employed. From this, by one washing with carbon bisulphide and several recrystallizations from petroleum spirit and benzene, beautiful white scales with blue fluorescence are obtained, which it is very difficult to obtain from ordinary crude anthracene. This is best accomplished after subliming at the lowest possible temperature and washing with ether to remove yellow colouring-matters; or it is dissolved in benzene and bleached by sun-light, in which case a little paranthracene is always formed. The safest way to obtain chemically pure anthracene is to reduce its derivatives by zinc dust*.

Pure anthracene forms shining white scales (clinorhombic prisms) with violet fluorescence. It fuses at 210° (Fritzsche, Berthelot) or 213° (Graebe and Liebermann), and sublimes at about the same temperature, with a pungent smell, yielding small, mica-like scales. At about 360° (certainly above phenanthrene) it boils, and yields a yellowish-white crystalline distillate; a portion, however, is always decomposed.

Pure anthracene is insoluble in water, little soluble in alcohol, more so in ether, benzene, and essential oils, as well as in boiling

* Auerbach, *Das Anthracen*, 2nd edit. p. 12.

alcohol, and especially in light tar-oils. According to Gessert*, 100 parts of

Alcohol cold	dissolve 0·6 of anthracene,
Benzene	„ 0·9 „
Carbon bisulphide „	1·7 „

According to Versmann†, at 15° 100 parts of

Alcohol, sp. gr. 0·800,	dissolves 0·591 part of anthracene,
„ „ 0·825,	„ 0·574 „ „
„ „ 0·830,	„ 0·491 „ „
„ „ 0·835,	„ 0·475 „ „
„ „ 0·840,	„ 0·460 „ „
„ „ 0·850,	„ 0·423 „ „
Ether	„ 1·175 „ „
Chloroform	„ 1·736 „ „
Carbon bisulphide	„ 1·478 „ „
Glacial acetic acid	„ 0·444 „ „
Benzene	„ 1·661 „ „
Petroleum	„ 0·394 „ „

According to Bechi‡, 100 parts of

Abs. alcohol at 16° dissolves 0·076; when boiling, 0·88 anthracene
Toluene „ 16°·5 „ 0·92; at 100°, 12·94 „

Its solution in benzene, when exposed to sunlight, soon deposits crystals of *paranthracene* which resist the action of solvents and concentrated acids and fuse at 244°, being reconverted into anthracene. Ordinary sulphuric acid with gentle heating dissolves anthracene and becomes of a greenish colour; at a higher temperature sulphonic acids are formed. Fuming sulphuric acid acts violently upon it. Oxidizing agents convert it into anthraquinone; reducing agents into hydrocarbons richer in hydrogen; nitric acid into nitro-compounds. Dissolved in benzene, along with picric acid, it yields ruby-coloured crystals, fusing at 170° and decomposed by alcohol. With dinitroanthraquinone (Fritzsche's reagent) it gives shining, rhomboidal, purple plates: if it is not quite pure, the plates are blue; if too impure, the reaction ceases altogether§.

* Dingler's Journal, cxcvi. p. 543.

† Ber. deutsch. chem. Ges. 1879, p. 1978. ‡ Chem. News, xxx. p. 204.

§ Fritzsche, Zeitschr. f. Chemie (2), iii. p. 289.

Anthracene Dihydride, $C_{14}H_{12}$.

Prepared by Graebe and Liebermann*; occurs in coal-tar; crystallizes in colourless plates, similar to naphthalene; fuses at 106° , begins to sublime at the same temperature, and distils at 305° without decomposition. It volatilizes already with aqueous or alcoholic vapours. It has a peculiar smell, especially at a higher temperature. It is insoluble in water, easily soluble in alcohol, ether, and benzene. In the solid state it shows no fluorescence; but its solutions have a blue fluorescence. It does not, like anthracene, yield a compound with picric acid.

Anthracene Hexahydride, $C_{14}H_{16}$.

Occurs along with the former; fuses at 63° , and boils at 290° ; its physical properties, solubilities, &c. are quite similar to those of the dihydride. A tetrahydride, which was formerly assumed, does not exist.

Monomethylantracene, $C_{15}H_{12} = C_{14}H_9 \cdot CH_3$.

Discovered in 1874 by Weiler†, and since then often examined, occurs in coal-tar in small quantities‡. It crystallizes from hot alcohol in thin, very bright, light-yellow scales; fuses at 200° (Weiler, Fischer) or $208-210^{\circ}$ (Wachendorff and Zincke); sublimes in greenish scales. Insoluble in water; little soluble in alcohol, ether, glacial acetic acid; easily soluble in chloroform, carbon bisulphide, and benzene. Nitric and sulphuric acids dissolve it slowly cold, more quickly when hot. With picric acid it yields a compound similar to that yielded by anthracene. The formula given by Laurent to his "paranaphthene" was also $C_{15}H_{12}$; but he cannot have had a pure compound before him.

Dimethylantracene, $C_{16}H_{14}$.

Was synthetically prepared by Van Dorp in 1872§, but not directly proved to exist in coal-tar. It resembles the preceding, and fuses at $224-225^{\circ}$.

* Ber. deutsch. chem. Ges. 1868, p. 187.

† Ibid. 1874, p. 1185.

‡ Japp & Schultz, *ibid.* 1877, p. 1049.

§ Ann. Chem. clxix. p. 207.

Phenanthrene, $C_{14}H_{10}$.

This isomer of anthracene was discovered at the same time by Graebe* and by Fittig and Ostermeyer†. It is found in the last fraction of the coal-tar oils, as a constant companion of anthracene, and forms a large portion of the crude anthracene. It is obtained from the raw material by many times repeated crystallization from alcohol, in which it is much more soluble than anthracene, and is also obtained in the factories in the purification of the latter. Moreover its lower boiling-point can be utilized for a preliminary separation of it from anthracene; its much lower fusing-point facilitates its identification.

Phenanthrene, when pure, crystallizes from alcohol in colourless scales with a faint blue fluorescence. It fuses at 99–100°, boils at about 340°, and sublimes in scales, less easily than anthracene. It dissolves at 13°·5 in 48 or 50 parts of alcohol (readily when hot); also in ether, benzene, glacial acetic acid, and carbon bisulphide. In alcoholic solution it yields with picric acid reddish-yellow needles, fusing at 143–145° and soluble in hot alcohol without decomposition. Nitric acid dissolves it, forming a nitro-compound; sulphuric acid at 100° forms a sulpho-acid. Bechi (*loc. cit.*) gives its solubility as follows:—In 100 parts of

Absolute alcohol, at 16° = 2·62, at 78° = 10·8 parts;

Toluene ,, 13°·5 = 33·02, ,, 100° in all proportions.

The structural formula of phenanthrene is now generally assumed

to be $\begin{array}{c} C_6H_4-CH \\ | \quad \parallel \\ C_6H_4-CH \end{array}$, i. e. a derivative of diphenyl.

Pseudophenanthrene, $C_{16}H_{12}$.

Fuses at 115°; discovered by Zeidler‡ in that portion of crude anthracene which is soluble in acetic ether, along with

Synanthrene, $C_{14}H_{10}$,

fusing at 189–195°. Nothing accurate is known of these bodies.

Fluoranthene, $C_{16}H_{10}$.

Syn. idryl. Discovered in 1877 by Fittig and Gebhardt§. It

* Ber. deutsch. chem. Ges. 1873, p. 861.

† Ann. Chem. cxlvi. p. 361.

‡ Chem. Centralbl. 1877, p. 566.

§ Ber. deutsch. chem. Ges. 1878, p. 2141.

probably stands in the same relation to fluorene ($C_{13}H_{10}$) as phenanthrene ($C_{14}H_{10}$) to diphenyl ($C_{12}H_{10}$). It accompanies pyrene in the highest-boiling fractions of coal-tar, and can be separated from pyrene only by many crystallizations from alcohol, preferably those of its compound with picric acid. It crystallizes from dilute alcohol in broad, shining, large plates; from a concentrated solution, in needles. It fuses at 109° , and afterwards sublimes. It dissolves with difficulty in cold alcohol, readily in ether, chloroform, benzene, carbon bisulphide, glacial acetic acid, and boiling alcohol; dissolved in concentrated sulphuric acid by gently heating, it gives it a greenish blue, at a higher temperature a blue, and ultimately a brown colour. With nitric acid it yields a trinitro-product; with picric acid in alcoholic solution, reddish-yellow needles fusing at 183° , and decomposed on boiling with water or addition of ammonia.

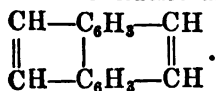
Pyrene, $C_{16}H_{10}$.

Laurent, in 1837, found it in coal-tar, but probably obtained it only in a very impure state. Graebe, in 1870, prepared it pure*. The fractions boiling above anthracene are extracted with carbon bisulphide, the filtrate is evaporated to dryness, the residue dissolved in alcohol, and a precipitate is produced by an alcoholic solution of picric acid, which is several times recrystallized from alcohol, and then decomposed by ammonia. The separated pyrene is recrystallized from alcohol. Colourless tables, fusing at 142° (according to Hintz† at 148°), subliming with difficulty, and boiling a good deal above 360° . Little soluble in cold alcohol, easily in carbon bisulphide, ether, benzene, and hot alcohol. Bechi (*loc. cit.*) states that its solubility in 100 parts of

Absolute alcohol, at $16^{\circ} = 1.37$, at $78^{\circ} = 3.08$ parts;

Toluene, „ $18^{\circ} = 16.54$, „ 100° very much.

It yields a nitro-product. Its picrate forms long red needles fusing at 222° , decomposed slowly by boiling water, at once by alkalis. Graebe regards it as phenylene-naphthalene, $C_{10}H_8(C_6H_4)$; it may also be represented as a diphenyl derivative in which the two nuclei are once more connected by two C_2H_2 groups,



* Ann. Chem. clviii. p. 285.

† Ber. deutsch. chem. Ges. 1878, p. 2142.

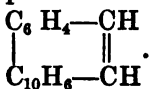
Chrysene, $C_{18}H_{12}$.

Discovered in 1817 by Robiquet and Colin when distilling amber, in 1837 by Laurent in coal-tar; afterwards investigated by many chemists. It is obtained in larger quantity only by distilling pitch as far as coke—mixed with pyrene as a yellow tough mass, sometimes as a dry powder. On extracting this mass with carbon bisulphide, it remains behind, and is recrystallized from hot glacial acetic acid or heavy tar-oil. The latter and oil of turpentine are its best solvents; carbon bisulphide dissolves only traces. Bechi states that its solubility in 100 parts of

Absolute alcohol, at $16^{\circ}=0.097$, at $78^{\circ}=0.17$ part;

Toluene, „ $18^{\circ}=0.24$, „ $100^{\circ}=5.39$ parts.

It usually forms loose, shining, yellow scales (rhombohedra with straight end face), whose colour, however, is caused by a tenaciously adhering mixture of another substance (chrysogen); in the state of perfect purity it is white. It fuses at 245° , sublimes similarly to anthracene, boils nearly at the same temperature as sulphur, but is at the same time partly decomposed. With picric acid and binitro-anthraquinone it forms compounds. In concentrated sulphuric acid it dissolves on being heated, with a purple colour; nitric acid yields nitro-products. It is a member of the series increasing by C_4H_2 , to which benzene, naphthalene, phenanthrene, chrysene, and picene belong; perhaps it is

*Chrysogen*.

Discovered in 1862 by Fritzsche* in coal-tar. It is the substance whose intense orange colour, even in the smallest quantity, imparts its tint to other bodies, *e.g.* to chrysene. Its formula is not yet established; it contains above 94 C per cent. It is isolated by frequent crystallization from light tar-oil and washing with ether and alcohol. It dissolves in 500 parts of boiling or 2500 parts of cold benzene, 2000 of boiling or 10,000 of cold glacial acetic acid. It is best obtained from boiling alcohol, in yellow scales, cohering like sal-ammoniac; the thinnest scales are pink, with gold-green lustre. Even $\frac{1}{3000}$ of it colours naphthalene an intense yellow; but its solutions are quickly bleached in the sun,

* Zeitschr. f. Chem. (2) ii. p. 139.

star-shaped groups of colourless needles being formed. It fuses at 280–290°, being partly decomposed; in concentrated sulphuric acid it dissolves without change.

Retene, $C_{18}H_{18}$.

Discovered in 1837 by Fikentscher and Trommsdorff, in coal-tar by Krauss*, studied especially by Fritzsche†. Shining, ointment-like scales, devoid of smell and taste, fusing at 98–99°, solidifying again at 90–95°, boiling at 350° without change, but volatilizing a little even at ordinary temperature, strongly in the water-bath. Sinks in cold water, but floats on hot. Insoluble in water, little soluble in cold alcohol, readily in hot alcohol, ether, fatty and essential oils. At a red heat it yields much anthracene.

Succisterene

is hardly a distinct chemical individual, but a mixture. Pelletier and Walter describe it as devoid of smell and taste, fusing at 160–162° and distilling above 300°, very little soluble in alcohol and ether. Analysis yielded 95·5 C and 5·6 H per cent.

Picene (Parachrysene), $C_{23}H_{14}$.

Discovered by Burg‡ in browncoal-tar, but very probably present in the heaviest tar-oils; identical with Rasenack's parachrysene§. It is very similar to chrysene, but even less soluble, viz. very little in boiling glacial acetic acid, benzene, and chloroform, best in coal-tar oils; boiling between 150° and 170°. Its fusing-point is higher than that of any other known hydrocarbon, viz. 337–339°, corrected = 345°. It dissolves in concentrated sulphuric acid, with a green colour.

Precisely the same body was found by Graebe and Walter|| in a product obtained by dry distillation of the purification residue of Californian petroleum. They found its formula = $C_{23}H_{14}$, which makes it a member of the series mentioned on p. 56. It fuses at 330–345°, and boils (as determined by Crafts's air-thermometer) at 518–520°. Hence also its boiling-point exceeds that of any other hydrocarbon of known formula.

* Ann. Chem. Pharm. cvi. p. 391.

† Journ. prakt. Chem. lxxv. p. 281.

‡ Ber. deutsch. chem. Ges. 1880, p. 1834.

§ Ibid. 1873, p. 1401; Wagner's Jahresh. 1873, p. 813.

|| Ber. deutsch. chem. Ges. 1881, p. 175.

Benzerythrene, C₂₄H₁₈.

Discovered by Berthelot*, prepared in the pure state by Schultz† and recognized as triphenylbenzene. Fuses at 307–308°. Small, white, shining, strongly electric scales. Little soluble in alcoholic or even boiling glacial acetic acid, more so in hot benzene; soluble in sulphuric acid, with a green colour.

Bitumens.

Badly characterized hydrocarbons, fusing with great difficulty, assumed to be present in coal-tar pitch. Carnelley‡ distinguishes two bitumens:—one boiling at 427–439°, which is readily soluble in benzene and carbon bisulphide, moderately in ether; and the other boiling above 439°, hardly soluble in benzene, but more easily in carbon bisulphide. The latter softened at 190°, began to fuse at 220°, but was not quite liquid till it reached 330°. Both were black masses with conchoidal fracture. Evidently Carnelley himself does not assume that those two bodies were homogeneous compounds.

OXYGENIZED COMPOUNDS.

*Water, H₂O.**Methylic Alcohol, CH₄O.*

Syn. wood-spirit, wood-naphtha. Boils at 63°; sp. gr. at 0° 0·818, at 20° 0·798. Occurs in wood-tar, and especially in crude wood-vinegar; not yet proved with certainty to occur in coal-tar.

Ethylic Alcohol, C₂H₆O.

Syn. spirit of wine. Boils at 78°·5; sp. gr. at 0° 0·8095, at 15°·5 0·7939. According to Witt§ it constitutes 2 per cent. of crude benzol; Vincent and Delachanal|| also found the same; but Krämer¶ doubts the fact. Possibly the difficulty arises from the circumstance that their "crude benzol" had already been treated with sulphuric acid and caustic-soda liquor, in which case it might happen that, from the ethylene dissolved in the tar, sulphovinic

* Ann. Chim. Phys. (4) ix. p. 458.

† Ber. deutsch. chem. Ges. 1878, p. 96.

‡ Journ. Chem. Soc. 1880, p. 714.

§ Chem. Centralbl. 1878, p. 415.

|| Compt. Rend. lxxvi. p. 840.

¶ Chemische Industrie, 1878, p. 126.

acid was formed, and decomposed by the alkaline treatment with formation of alcohol. Watson Smith also explains the formation of alcohol in this way; but he could only find small traces of alcohol in London benzene.

Acetic Acid, $C_2H_4O_2$.

Boils at 119° ; sp. gr. at 15° 1.057. Extremely important as is its occurrence in wood-tar, it seems to be nearly, if not quite, absent from coal-tar. Vincent and Delachanal (*loc. cit.*) found it on distilling crude benzol with alkali, as a product of the decomposition of methylic cyanide.

Phenol (Carbolic Acid), C_6H_6O .

Syn. phenylic acid, phenylic alcohol. Discovered by Runge*, more exactly examined by Laurent, and subsequently by many chemists. It occurs much more abundantly in coal-tar than in other tars. In the pure state it forms long white needles, fusing at $42^\circ.2$ into a clear, colourless liquid, and boiling at 182° without decomposition. Ordinary "pure" phenol, which contains traces of cresol or water, fuses at about $35^\circ.5$, and boils at 188° . Hence the phenol examined by Adrieenzt†, and considered exceptionally pure, which fused at $37^\circ.8$, solidified at $34^\circ.3$, and boiled at $183^\circ.3$ – $184^\circ.1$, was not absolutely pure. Really pure phenol, fusing at 42° , is less deliquescent than that melting at 35° , which contains a little cresol. In damp air phenol absorbs water, and its fusing-point is lowered by the formation of a *hydrate*, C_6H_6O, H_2O , containing 16.07 per cent. of water and fusing at $17^\circ.2$ ‡. It seems to be the same as that obtained by Calvert on exposing a mixture of 4 parts of phenol with 1 part of water to a temperature of 4° , although he states its fusing-point to be 16° , and its formula $2(C_6H_6O), H_2O$. The hydrate begins to lose water at 100° , and thus gradually arrives at the boiling-point of anhydrous phenol.

In very damp air the hydrate absorbs still more water, and then remains liquid. If to phenol as much water is added as can be mixed with it, the resulting liquid contains about 27 per cent. water, almost exactly corresponding to the hydrate $C_6H_6O, 2H_2O$.

* Poggend. Ann. xxi. p. 69, xxxii. p. 308.

† Ber. deutsch. chem. Ges. 1873, p. 443.

‡ Allen, The Analyst, iii. p. 319.

But on shaking this liquid with 4 vols. of benzene, it gives up the whole of its phenol to the latter, the water being separated (Allen).

The specific gravity of phenol at 18° is 1·065; its expansion for the temperature t at the pressure of 760 millim. is stated by H. Kopp as follows:

$$V_t = 1 + 0\cdot0006744t + 0\cdot000001721t^2 - 0\cdot00000000050408t^3.$$

Adrieenz (*loc. cit.*) gives the following table of the volumes of phenol:—

Temp.	Sp. gr.	Volume.
40	1·05433	1·01504
50	1·04663	1·02259
60	1·03804	1·03036
70	1·02890	1·04028
80	1·01950	1·04984
90	1·01015	1·05951
100	1·00116	1·06899

In spite of being deliquescent, phenol is not very easily soluble in water, but is so in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerine, &c. The usual statement is that phenol dissolves in 20 parts of water; and some give even a much higher figure. But Allen states that liquid aqueous carbolic acid dissolves in 11·1 times its volume of cold water, corresponding to pure phenol dissolving in 10·7 times its weight of water or to the aqueous solution containing 8·56 per cent. According to Hamberg*, pure carbolic acid (fusing-point 40–41°, solidifying-point 39°, boiling-point 180–180°·5) dissolves at 16° or 17° in 15 parts of water, and at 40° in two vols. of liquor ammoniæ of sp. gr. 0·96 (forming a clear liquid which turns milky at 17° or 18°). Other statements, attributing to it a less considerable solubility, must be explained by the presence of cresol, which lowers the solubility. The aqueous solution does not redden litmus; benzene, ether, carbon bisulphide, or chloroform abstracts phenol from its aqueous solution. Cold petroleum-spirit dissolves but little of it (compare below).

* Ber. deutsch. chem. Ges. 1871, p. 751.

The smell of carbolic acid is very similar to that of wood-tar creosote (that is, smoky) ; but (like the taste) it is less pronounced in very pure phenol than in impure ; so that in the former case it can be masked by a few drops of geranium oil, which also keep it always liquid. The taste of phenol is burning and sweet at the same time : it violently acts upon the epidermis, turning it white and hardening it or making it shrink. Hence it must be cautiously handled ; rubbing with a fatty oil lessens the pain and the bad consequences of an external contact with it. Internally it acts of course as a poison, both by its corrosive action on the epithelium and by its property of coagulating albumen ; it seems to act upon the nervous system by paralyzing the nerve-centres. According to Allen even a momentary contact of strong acid with an extended surface of the lower parts of the body is mostly fatal, but on the arms it acts comparatively little.

The poisonous and coagulating properties of phenol are very specially exhibited by its preventing the development of lower organisms ; this has made it one of the most important agents for the prevention of fermentation and putrefaction, for Lister's treatment of wounds, &c. ; and its technical application, apart from its employment in the manufacture of a few colouring-matters, of salicylic acid, &c., is exclusively owing to its antiseptic property.

Phenol not quite pure turns red more or less quickly, especially under the influence of air and light. The cause of this is not quite certainly known ; perhaps it is the formation of rosolic acid by the influence of traces of mineral acids, in the presence of homologues and of oxygen.

The following reactions are characteristic. A drop of a dilute solution of phenol gives with a solution of 1 part of molybdic acid in 10 of concentrated sulphuric acid a yellow-brown colour, soon turning purple. Heating to not above 50° assists the reaction. Since many other bodies cause the reduction of molybdic acid, this reaction is interfered with by them.—By addition of ferric chloride (not in excess !) 1 part of phenol in 1000 or at most 1500 (not 3000, as usually stated) can be recognized by a purple colour ; but some neutral salts interfere with this, and, on the other hand, other compounds show the same reaction.—Twenty cubic centim. of a solution of 1 part of phenol in 10,000 water, mixed with a very little liquor ammoniæ and then with a little

fresh saturated chlorine-water or, preferably bromine-water, produce a deep indigo-blue colour. This reaction is very stable, the colour remaining unchanged for days and weeks even in the open air.—On heating phenol solutions with $\frac{1}{3}$ to $\frac{1}{2}$ their bulk of a 10- or 15-per-cent. solution of mercurous nitrate, a pink colour appears, which is strongest 1 or 2 hours afterwards. This reaction is almost as sensitive as the next, and remains for some time.—Even 1 part of phenol in 80,000 water can be discovered by adding fresh bromine-water, a white crystalline precipitate of tribromphenol ($C_6H_3Br_3O$) being formed, but in the case of very dilute solutions not till after some time.

The quantitative estimation of phenol will be described in Chapter VIII.

Phenol is the type of a whole class of bodies which stand as it were midway between alcohols and acids. Hence the older and industrially most usual name, "carbolic acid," is hardly used in scientific writings. The phenols form a class by themselves, viz. those aromatic compounds in which the hydrogen atoms of benzene nuclei are replaced by hydroxyl (OH). The hydrogen of the latter is easily replaced by metals or alcoholic radicals; but the other characteristics of a real acid are absent.

Phenol is consequently more soluble even in dilute alkaline solutions than in water, with formation of easily soluble and crystallizable compounds (*e.g.* with potash, soda or ammonia) called carbolates or phenylates ($C_6H_5, ONa, \&c.$). These compounds are not very stable; they are not decomposed by dilution with water, but by heating in the dry state, which liberates the phenol. Ether and alcohol dissolve these compounds. Hence the phenols can be separated from the indifferent tar-oils by treatment with an alkali.

Concentrated sulphuric acid also dissolves phenol with formation of sulphonic acids, and thus removes it from tar-oils, which, however, easily retain a little of the sulphonic acid. Nitric acid yields nitro-products, one of which is technically important, viz. picric acid, $C_6H_2(NO_2)_3OH$. In the presence of bodies which can furnish methane carbon, along with free mineral acids and oxygen, rosolic acid, $C_{19}H_{14}O_8$, is formed. Upon this is based the technical preparation of coralline from phenol, oxalic acid, and sulphuric acid—and perhaps also the reddening of impure phenol, cresol [$C_6H_4(CH_3)(OH)$] furnishing the methane carbon.

Cresols, $C_7H_8O = C_6H_4(CH_3)(OH)$.

Syn. oxytoluene, cresylic acid.

There are three isomers of this formula; coal-tar seems to contain a mixture of them. The isomers cannot be prepared in the pure state except synthetically.

Orthocresol (1, 2) fuses at 31° , and boils at $185-186^\circ$.

Paracresol (1, 4) forms colourless prisms, fusing at 36° and boiling at 198° . It smells like phenol, and is little soluble in water. Its aqueous solution, like that of metacresol, is coloured blue by ferric chloride.

Metacresol (1, 3) boils at $195-200^\circ$; it is a thick liquid, not solidifying at -80° .

Commercial cresylic acid, a mixture of the isomers, is a colourless, refractive liquid, does not solidify at -80° , has a specific gravity of 1.044, is much less soluble in water and alkalis, and boils at a higher temperature than carbolic acid, about $185-203^\circ$. It gives the same reaction with ferric chloride as carbolic acid, and is even more strongly acted upon by strong sulphuric and nitric acids. With bromine it gives a tribromo-compound, $C_6HBr_3(CH_3)(OH)$, liquid at ordinary temperature. Its antiseptic properties are even more strongly marked than those of carbolic acid.

Allen has given the following table on the differences between carbolic acid (Calvert's No. 1) and cresylic acid (prepared from Calvert's No. 5 by fractionating):—

	CARBOLIC ACID.	CRESYLIC ACID.
1. Melting-point	Solid at ordinary temperature; liquefied by addition of water; both absolute and hydrated acid solidified by freezing-mixture.	Liquid at ordinary temperature; neither absolute nor hydrous acid is solidified by freezing-mixture.
2. Boiling-point	182°	$198-203^\circ$.
3. Solubility of hydrous acid in cold water.	1 vol. in 11	1 vol. in 29.
4. Solubility in strong solution of ammonia (sp. gr. 0.880).	Completely and readily soluble in equal volume; solution not precipitated by addition of less than $1\frac{1}{2}$ volume of water.	Almost insoluble; requires 16 volumes; then forms crystalline scales.

	CARBOLIC ACID.	CRESYLIC ACID.
5. Reaction with solution of caustic soda (free from alumina) containing 6 per cent. NaOH.	Completely soluble in equal volume. Addition of the alkali solution, even up to 6 volumes, causes no change.	Insoluble in small proportions. With large excess it disappears and forms crystalline scales.
6. Reaction with solution of caustic soda containing 9 per cent. NaOH.	Completely and readily soluble in equal volume. On addition of any proportion of water up to 7 volumes the liquid remains clear, but is precipitated by 8 measures of water. Soluble in 2 measures of soda, and not precipitated by less excess than 5 or 6 measures.	Soluble in equal volume, but precipitated by adding a few drops of water, the original volume separating when water is added amounting to 1 measure. The solution in soda is reprecipitated when the alkali solution is added to the extent of $3\frac{1}{2}$ measures.
7. Reaction with petroleum-spirit.	Absolute acid is miscible with hot petroleum-spirit in all proportions. Miscible with only $\frac{1}{2}$ vol. of cold petroleum-spirit, precipitated by greater proportion. With 3 vols. of petroleum-spirit, bulk unchanged; upper layer contains carbolic acid, which crystallizes out on sudden cooling by freezing-mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solution in 3 measures of petroleum-spirit.
8. Behaviour with glycerine of sp. gr. 1.258.	Miscible in all proportions. One measure of carbolic acid with an equal volume of glycerine is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 vols. of water being the maximum for a sample containing 25 per cent. cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerine, is completely precipitated by 1 measure of water.

According to this, cresylic acid is less soluble than carbolic acid in water, ammonia, glycerine, and caustic-soda liquor, but more easily in petroleum-spirit. Hence, though the presence of considerable quantities of cresylic acid can be discovered in carbolic acid, the utilization of those reactions for a quantitative estimation

of these bodies is out of the question. An approximate estimation of this kind will be described in Chapter VII.

Xylenols (Xenols), $C_6H_{10}O = C_6H_3(CH_3)_2OH$.

Of the six xylenols admitted by theory, four are known. In coal-tar probably several of these occur; it is also probable that the "*phlorol*" from beach-wood tar (boiling at 220°) is such a mixture*. The pure compounds have been obtained synthetically.

Orthoxenol (1, 2, 4) = $C_6H_3(CH_3^1)(CH_3^2)(OH^4)$. Fuses at 61° and boils at 225° . Crystallizes from water in long needles, from dilute alcohol in orthorhombic octahedra; yields a soluble sodium salt in thin needles.

Metaxenol I. (1, 2, 3) = $C_6H_3(CH_3^1)(CH_3^2)(CH_3^3)$. Long needles or plates, fuses at $74^\circ.5$, and boils at $211-212^\circ$ (Jacobsen), or at 73° and 216° respectively (Fittig and Hoogewerf).

Metaxenol II. (1, 3, 4) = $C_6H_3(CH_3^1)(CH_3^3)(OH^4)$. A colourless, strongly refractive liquid of sp. gr. 1.0362 at 0° , does not solidify in the cold, boils at $211^\circ.5$, little soluble in water, miscible with alcohol and ether. Its alcoholic solution is turned green by ferric chloride, its aqueous solution blue, whilst the other xenols do not give any reaction with that salt.

Paraxenol (1, 3, 4) = $C_6H_3(CH_3^1)(OH^3)(CH_3^4)$. Colourless crystals, very like metaxenol I., fuses at $74.5-75^\circ$, boils at $211.5-213^\circ.5$, sp. gr. at 18° 0.9709. Solubility like that of the above.

There are higher phenols known, viz.:—*mesitylol*, $C_9H_{11}.OH$, boiling at 220° ; *pseudocumenol*, $C_9H_{11}.OH$, boiling at 240° ; *thymol*, $C_{10}H_{13}.OH$, boiling at 230° ; *carvacrol* (same formula), boiling at $233-235^\circ$; but their existence in coal-tar is not proved.

Neither are the oxyphenols proved to occur in coal-tar, whilst in wood-tar they and their ethers are most important, especially *pyrocatechin*, $C_6H_4(OH)_2$, *homopyrocatechin*, $C_6H_3(CH_3)(OH)_2$, the methylic ether of the former (*guaiacol*) and that of the latter (*creosol*).

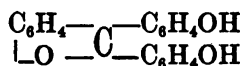
Rosolic acid, $C_{19}H_{14}O_8$.

Syn. aurin. Discovered in 1834 by Runge† in coal-tar; after-

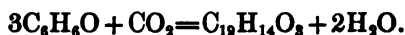
* Marasse, Ann. Chem. Pharm. clii. p. 75.

† Pogg. Ann. xxxi. pp. 65, 512, xxxii. pp. 308, 323.

wards synthetically prepared at the same time by Persoz* and by Kolbe and Schmitt†, but in a very impure state, by treating phenol with oxalic acid and sulphuric acid. Since then it has been examined by many prominent chemists; its constitution, and even its formula, was only ultimately recognized in 1878, at the same time by E. and O. Fischer and by Graebe and Caro. The rosolic acid from phenol, which is probably the same as that contained in tar, has now generally received the formula $C_{19}H_{14}O_8$, or, structurally,



i. e. a derivative of triphenylmethane, in which three hydrogen atoms are replaced by hydroxyl, and from which one molecule of water is abstracted‡. Hence it is formed if three phenol remainders can attach themselves to a carbon atom of the fatty series (methane carbon); and it actually forms an inner anhydride of the trioxo-triphenylmethane-carbinol. It is now pretty generally assumed that its formation from phenol, oxalic acid, and sulphuric acid is caused by the liberation, from the oxalic acid, of CO_2 , which in the nascent state gives up its oxygen to oxidize 4H of the phenols and attaches the remainders to the vacant bonds of carbon, thus:—



(The accessory reactions which take place in the formation of corallin, *i. e.* the crude product, must be left untouched here.)

We have already (p. 61) pointed out that the conditions for the formation of rosolic acid are given when, besides phenol itself, its higher homologues containing the methyl group CH_3 are present, and if at the same time mineral acids can act upon it by separating water; but there must be an oxidizing action as well: thus,



Perhaps this explains why the reddening of phenol requires the presence of air, as well as the reddening of impure naphthalene, which in any case contains some unchanged phenol.

* French Patent No. 54,910 of 21st July, 1881.

† Ann. Chem. Pharm. cxix. pp. 119, 169.

‡ Graebe and Caro proposed to keep the name *aurin* for this compound, and to apply that of *rosolic acid* to the higher homologue, made from rosaniline; but this has not been generally accepted.

It would then be possible that the rosolic acid found by Runge in coal-tar was only formed by acid treatment of the products. (Whether a mineral acid is absolutely necessary or not, is not yet proved.) He obtained it by exhausting the residues from the distillation of phenol by water, dissolving in $\frac{1}{3}$ of their weight of alcohol, and mixing with lime. Thus he obtained a pink solution of calcium rosolate and a brown precipitate of calcium brunolate. From the former rosolic acid is precipitated by acetic acid, and purified by repeated solution in milk of lime and precipitation by acetic acid till no more calcium brunolate separates. Ultimately, by dissolving in alcohol and evaporating, a hard, glassy, orange-coloured mass is obtained, whose valuable dyeing-properties were pointed out very emphatically by Runge, but were first utilized a generation afterwards.

That an oxidation process takes place in this case seems to be proved by the fact that slow heating of the heavy tar-oils with lime in the presence of air much increases the yield of rosolic acid *. Angus Smith went even further, by heating phenol, caustic alkali, and manganese dioxide †.

Brunolic acid (?).

Runge thus named an acid which he isolated from the brown precipitate filtered from the solution of calcium rosolate. It was an asphalt-like, glassy mass, undoubtedly a mixture of different chemical compounds.

SULPHURETTED COMPOUNDS.

Hydrogen sulphide, H_2S .

Ammonium sulphide, $(NH_4)_2S$.

Ammonium sulphocyanide, $(NH_4)NCS$.

Sulphur dioxide, SO_2 .

These must occur in coal-tar, as they are always present in gas-liquor (compare the last Chapter).

Carbon bisulphide, CS_2 .

Boiling-point 47° . Sp. gr. 1.272. Was found in crude benzol by Vincent and Delachanal †; it had often been assumed to exist

* Tschelnitz, Wiener Akad. Ber. Jan. 1858, xxiii. p. 169.

† Chem. Gaz. 1858, no. 20.

‡ Compt. Rend. lxxxvi. p. 340.

in tar, as it is always found in the gas. Watson Smith has found 6 per cent. of CS_2 in the first runnings of rectified benzol from London gas-tar.

Carbon oxysulphide, COS ,

has not yet been found in tar, but is sure to exist dissolved in it, since all conditions are present for its formation. It is a colourless gas, smelling of carbonic anhydride and a little of hydrogen sulphide, of very faintly acid reaction. It is extremely inflammable, and with sufficient oxygen yields CO_2 and SO_2 ; with insufficient oxygen or on cooling, it yields only CO_2 and S : $\text{COS} + \text{O} = \text{CO}_2 + \text{S}$.

Mercaptans

or similar sulphuretted compounds having a disagreeable smell are evidently present in coal-tar. The alliol of which Mansfield stated the boiling-point to be $70-80^\circ$, and of which he obtained 30 to 40 grams from 50 litres of tar, is perhaps a mixture of such compounds, although carbon bisulphide might be thought of as well. Vohl* has found, in crude benzene, sulphuretted bodies boiling below 80° .

		Sp. gr.
Methyl mercaptan, $\text{CH}_3 \cdot \text{S}$	boils at 20°	
Methylic sulphide $(\text{CH}_3)_2\text{S}$	„ 41°	0.845
Ethyl mercaptan, $\text{C}_2\text{H}_5 \cdot \text{SH}$	„ 36°	0.831
Ethylic sulphide $(\text{C}_2\text{H}_5)_2\text{S}$	„ 91°	0.825
&c.		

Free Sulphur

has been found by Kehlstadt † in the distillates of coal-tar. It is probably formed from SO_2 and H_2S under the action of water.

NITROGENIZED COMPOUNDS.

A. BASIC.

Ammonia, NH_3 ,

has been already mentioned as ammonium sulphide and sulphocyanide. It occurs also as carbonate, and forms the most important constituent of gas-liquor. A colourless gas, of the well-known pungent smell, sp. gr. 0.5888, condenses at -40° to a liquid, and solidifies at -70° . Its ready solubility in water, the strongly basic properties of this solution, &c. are universally known.

* Dingler's Journal, clxviii. p. 40.

† Ber. deutsch. chem. Ges. 1880, p. 1345.

Substituted Ammonias

of the fatty series occur probably in gas-liquor, and consequently in tar. We shall only quote the boiling-points &c. of the lowest members.

Methylamine, $\text{NH}_2(\text{CH}_3)$ is a gas. 1 vol. water at 12° absorbs 1040 vols. of it. It is inflammable; it smells like fish and ammonia at the same time.

Dimethylamine, $\text{NH}(\text{CH}_3)_2$ boils at $8-9^\circ$; readily soluble in water. Smell strongly ammoniacal.

Trimethylamine, $\text{N}(\text{CH}_3)_3$ boils at $9^\circ.3$; readily soluble in water. Smells of ammonia and herring-brine, in which it occurs abundantly.

Ethylamine, $\text{NH}_2(\text{C}_2\text{H}_5)$, boils at $18^\circ.7$; readily soluble.

Diethylamine, $\text{NH}(\text{C}_2\text{H}_5)_2$, boils at $57^\circ.5$; readily soluble.

Triethylamine $\text{N}(\text{C}_2\text{H}_5)_3$, boils at 91° ; little soluble.

The higher members and the extremely numerous mixed amines cannot be noticed here.

Cespitine, $\text{C}_6\text{H}_{13}\text{N}$,

is a base of unknown constitution, isomeric with amylamine and boiling at the same temperature (95°). It was discovered by Church and Owen. A colourless oil of strong smell, less disagreeable than that of amylamine; readily soluble in water, but not in concentrated solution of caustic soda. Lighter than water. Church and Owen suppose in it a trivalent radical $(\text{C}_6\text{H}_{13})'''$.

Aniline, $\text{C}_6\text{H}_5 \cdot \text{NH}_2$.

Syn. phenylamine, amidobenzene, &c. Discovered in 1826 by Unverdorben, (in coal-tar) 1834 by Runge (who called it kyanol). A colourless liquid, very soon turning yellow, then red or brown, of a peculiar faint smell and burning taste. Solidifies at -8° (some say, not even at -20°), and boils at 182° ; the vapour burns readily. Sp. gr. at $16^\circ = 1.020$. It possesses poisonous properties, especially for smaller animals. Water dissolves about 2 per cent.; and it dissolves some water itself. Readily soluble in alcohol, ether, acetone, carbon bisulphide, hydrocarbons, &c. It dissolves sulphur, phosphorus, camphor, rosin. The aqueous solution has only faintly basic properties, and does not even turn red litmus blue; but at a higher temperature it expels ammonia from its salts, whilst in the cold it is precipitated by ammonia. With

chloride of lime it turns purple; with potassium bichromate, blue. Its aqueous solutions precipitate the oxides from the salts of iron, zinc, and aluminium. With the mineral acids it forms salts which are readily soluble in water and alcohol and crystallize well. They are white when quite pure, but redden quickly in the air and assume a faint smell.

Immense as is the importance of the aniline made from coal-tar benzol, its direct occurrence in coal-tar is yet of small moment. Here it is practically only an impurity, from which the hydrocarbons must be freed by acid treatment; neither does it seem feasible to extract at a profit the small quantity present in coal-tar.

According to Watson Smith*, aniline occurs in all distillates of coal-tar, principally (as might be presumed from its boiling-point) in the light oils of sp. gr. 0.900 to 1.000.

The *homologues of aniline* (*toluidine* &c.) have not yet been proved to exist in coal-tar.

Pyridine Series.

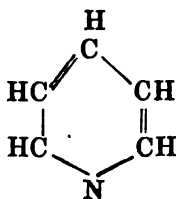
This series embraces a number of bases of the formula $C_nH_{2n-3}N$, from pyridine to viridine. Their constitution is still unknown; they are isomers of aniline &c. They are very stable, even towards oxidizing agents. They have been quite recently re-investigated by A. W. Hofmann (Ber. deutsch. chem. Ges. 1881, p. 1497). They occur chiefly in the tar-oils of sp. gr. 0.900 to 0.990.

Pyridine, C_5H_5N .

Discovered by Anderson in bone-tar, by Greville Williams in coal-tar. Its synthesis has not yet been achieved with certainty. A colourless, mobile liquid of penetrating smell. Sp. gr. at 0° 0.9858; boils at $116^\circ.7$ (Anderson) or 115° (Thenius). Miscible with water in all proportions, and reprecipitated by caustic potash or soda. Turns red litmus blue, gives off white vapours with hydrochloric acid, precipitates cold the salts of zinc, iron, manganese, aluminium. Resists the action of fuming nitric and chromic acid. With the acids it forms stable salts readily soluble in water and alcohol, which can be dried at 100° , and hardly turn brown in the air.

Its formula is now mostly given as:—

* Journ. Chem. Soc. 1874, p. 853.

*Picoline*, C_6H_7N .

Syn. odorine. Isomeric with aniline. Discovered by Unverdorben in bone-oil, by Anderson in coal-tar. A colourless, mobile liquid of penetrating smell. Boils at 135° ; sp. gr. at 0° 0.9613 (Anderson), at 22° 0.933 (Thenius). Its solubility, salts, and basic properties resemble those of pyridine.

Lutidine, C_7H_9N .

A colourless oil, of faint aromatic smell; boils at $154^\circ.5$; sp. gr. at 0° 0.9467. Soluble in 3 or 4 parts of water; on heating it is partly re-precipitated from this solution.

Collidine, $C_8H_{11}N$.

A colourless, aromatically smelling liquid, boiling at 179° , almost insoluble in water; sp. gr. at 0° 0.921.

Parvoline, $C_9H_{13}N$.

This, as well as the three following members, is very little known. Boils at 188° , sp. gr. 0.966.

Coridine, $C_{10}H_{15}N$.

Discovered by Thenius. A colourless liquid of faint smell, like leather; boils at 211° , does not solidify at -17° ; sp. gr. at 22° 0.974. Little soluble in water, readily in alcohol, ether, &c. Yields crystalline salts.

Rubidine, $C_{11}H_{17}N$.

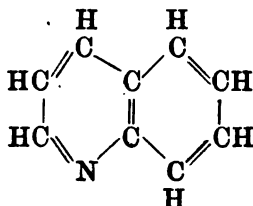
Discovered by Thenius. A colourless oil of faint smell, boils at 230° , turns viscid at -17° , insoluble in water, soluble in alcohol, ether, &c. Sp. gr. at 22° 1.017. It precipitates some oxides from their salts. Its salts do not crystallize well, and turn pink in the air; chloride of lime turns it pink; it stains pine wood, moistened with hydrochloric acid, a red colour.

Viridine, $C_{12}H_{19}N$.

Discovered by Thenius. A yellowish oil, of sweet aromatic smell; boils at 251° , at -17° not yet solid. Does not colour in the air; very little soluble in water. Sp. gr. at 22° 1.024.

Leucoline Series.

(Quinoline series.) Especially studied by Greville Williams*. Probably the bases obtained from coal-tar are not identical with those obtained by distilling cinchonine with caustic potash. Their chemical constitution is not yet known with complete certainty; that of quinoline is usually represented as

*Leucoline*, C_9H_7N .

Discovered in 1884 by Runge; isomeric with quinoline, which it resembles very much in its properties. The latter boils at 238° and has a specific gravity of 1.081, a penetrating smell, and burning taste. It is little soluble in water, readily in alcohol and ether. Turns resinous on standing in the air; yields many salts.

Iridoline, $C_{10}H_9N$.

Isomeric with *lepidine* from cinchonine. Boils between 252° and 257° . Yields crystallizable salts with nitric, hydrochloric, and chromic acids, &c.

Cryptidine, $C_{11}H_{11}N$.

Boils at 274° ; isomeric with *dispoline* from cinchonine. Can be separated from the preceding only by crystallization of the platinum double salt. Properties unknown.

In the products from cinchonine there occur more bases of this series, up to $C_{16}H_{21}N$; but these have not been found in tar.

* Chem. Soc. Journ. [2]. i. p. 375; Chem. News, i. p. 15.

General Process for preparing the Bases from Coal-tar.

A large quantity of tar is agitated with a mixture of one part of sulphuric acid and two parts of water, if necessary, repeatedly. After some rest the clear liquid is drawn off and boiled in an open vessel till all pyrrol is volatilized, which is proved by the fact that a bit of fir wood, moistened with hydrochloric acid, does not redden. The liquid is now passed through linen cloth, caustic-soda solution in excess added to it, and the whole distilled. The aqueous vapour carries away the bases; if the distillate be not concentrated enough, it is saturated with solid caustic potash, avoiding too much heating; and the oily mixture of bases, separating at the top, is decanted. If it contains aniline, fuming nitric acid is cautiously added and the mixture gradually heated to boiling, whereby the aniline is destroyed; the other bases remain intact. Water is added, the precipitate filtered off, and the filtrate again saturated with caustic potash. The decanted oil contains much water, which is absorbed by solid caustic potash; this must be done completely, since otherwise the boiling-points of the more volatile bases are much changed. Now the oil is methodically fractionated, sometimes as many as 20 times, till the boiling-points are constant.—Greville Williams destroys aniline and its homologues by heating with potassium nitrite and hydrochloric acid, and then proceeds as above.

Acridine, C₁₃H₉N.

Discovered by Graebe and Caro * in crude anthracene. Isomeric with carbazol, but basic. Obtained by extracting crude anthracene with dilute sulphuric acid, precipitating by potassium chromate, purifying the chromate by recrystallization, precipitating the base by ammonia, and recrystallizing the same from hot water. Or the hydrochlorate is recrystallized and decomposed by ammonia. Acridine crystallizes in orthorhombic prisms, colourless if very small, brown if larger. It fuses at 107°, distils at 360° without change, sublimes at 100°, and is carried over by aqueous vapour. It is little soluble in cold, more so in hot water, readily in ether, alcohol, carbon bisulphide, and hydrocarbons. It possesses a faint alkaline reaction; but even very dilute solutions of its salts on the skin cause acute stinging; its dust in the most minute quantity

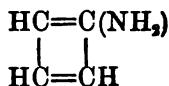
* Journ. f. prakt. Chem. [2] ii. p. 183; Ber. deutsch. chem. Ges. 1872, p. 15.

causes most violent sneezing. Sulphuric acid attacks it only at 200°; hydrochloric acid and caustic potash do not begin to attack it at 280°; zinc dust, soda-lime, many oxidizing agents not at all. Nitric acid forms nitro-compounds. With the acids it forms salts, all of yellow colour, easily soluble and crystallizable. Their dilute solutions fluoresce strongly with a blue colour, more concentrated ones green, the very concentrated ones not at all.

B. NOT BASIC.

Pyrrrol, C_4H_5N .

Discovered by Runge, isolated in the pure state by Anderson. Prepared by distilling the oils (p. 73) after saturation with sulphuric acid, and fractionating. A colourless liquid of chloroform-like smell and burning taste; boils at 133°; sp. gr. 1.077. Little soluble in water, insoluble in alkalies, readily soluble in ether and alcohol, slowly in dilute acids. In the air it turns brown, but is again rendered colourless by distillation. It tinges a piece of fir wood moistened with hydrochloric acid, first pink, then crimson. It is indifferent towards most reagents, but is perhaps very slightly basic. No salts of it are known. With potash it forms a compound not decomposable by heat, but at once by water. Its constitution is explained by a closed chain of four carbon atoms, thus,



Cyanogen Compounds.

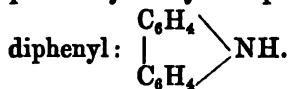
We have already mentioned ammonium sulphocyanide. According to Vincent and Delachanal* tar contains also *methylic cyanide* (aceto-nitrile), $\text{CH}_3\text{—C}\equiv\text{N}$, which under the action of alkalies takes up the elements of water and yields acetic acid and ammonia. They found it in Paris benzol, together with carbon bisulphide, in that part of benzol which boils below 80°.

Methylic cyanide boils at 77°; sp. gr. 0.835. A colourless liquid of peculiar, not disagreeable smell, miscible with water in all proportions, and burning with a purple-bordered flame.

* Compt. Rend. lxxvi. p. 340.

Carbazol, $C_{12}H_8N$.

Syn. imidodiphenyl; isomeric with acridine. Discovered by Graebe and Glaser* in the residue from the purification of anthracene by caustic potash (Chapter VI.), in which a combination of it with potash, decomposable by water, is contained. It is always a considerable constituent of crude anthracene. Its properties are very similar to those of a hydrocarbon; like the hydrocarbons, it forms a compound with picric acid, fusing at 182° in large red prisms, which can be employed for preparing pure carbazol. The latter can also be purified by recrystallizing or subliming. It forms white scales or plates, insoluble in water, a little soluble in cold alcohol, ether, benzene, chloroform, more so at a higher temperature: 100 parts of toluene dissolve at $16\frac{3}{4}^\circ$ 0.55, at 100° 5.46 parts; 100 parts absolute alcohol at 14° 0.92, at 78° 3.88 parts. Fusing-point 238° ; it sublimes readily, and boils near 355° . In pure cold sulphuric acid it dissolves, the solution having a yellow colour; the most minute traces of nitric acid, chromic acid, chlorine, or other oxidizing agents produce an intense green colour. Water precipitates it unchanged from the cold solution in sulphuric acid; by heating, a sulphonic acid is formed. Nitric acid yields nitro-products. Carbazol is not changed by igniting with soda-lime, caustic lime, zinc-dust, &c.; on igniting with potash-lime a portion is decomposed, ammonia being formed. It has no basic properties, and forms no salts with acids, but a compound with acetyl and with potassium, in which the hydrogen of the imido-group is replaced by acetyl or potassium. It is the imido-compound of

*Phenylnaphthyl-carbazol*, $C_{16}H_{11}N$.

Syn. imidophenylnaphthyl. Discovered by Brunck, examined by Graebe and Knecht† (who obtained it also synthetically). Is obtained by subliming the residue from distilling crude anthracene. Intensely yellow, but only by the admixture of some unknown substance; for on being fused with potassium hydrate it turns white. Almost insoluble in cold, very little soluble in boiling

* Ann. Chem. Pharm. clxiii. p. 343, clxx. p. 88.

† Ber. deutsch. chem. Ges. 1879, pp. 341, 2241.

benzene or glacial acetic acid, more soluble in hot aniline. Toluene and absolute alcohol, when cold, dissolve next to nothing of it; boiling toluene dissolves 0·89–0·57, alcohol 0·25 per cent. The solutions have an intense blue fluorescence. It fuses at 380°, and has a higher boiling-point than sulphur. Its behaviour to sulphuric acid &c. resembles that of carbazol.

CHAPTER III.

THE APPLICATIONS OF COAL-TAR WITHOUT DISTILLATION.

BEFORE gas-tar was distilled on a manufacturing scale in order to isolate valuable substances contained in it, of course it had to be employed in other ways, either in the raw state or thickened by evaporation. Even later on the tar could not, and in some places up to this day cannot, be distilled to advantage, principally owing to the cost of carriage; and it was necessary to find other uses for it, in order to get rid of it.

The most obvious plan was to try whether gas-tar could not be employed for *making gas* itself, by passing it through red-hot tubes, or by distilling it and similarly treating the vapour. This was the intention of the process of Koechlin, Duchatet, and Perpigna *, that of A. Bernard † (who ran the tar upon the coke remaining in the gas-retorts), that of *Droinet* ‡ (who moulded the tar, mixed with ashes, coal-dust, saw-dust, clay, &c., into compact lumps which were heated in ordinary gas-retorts), that of Isoard § (whose tar-gas, prepared by superheated steam, contained, according to Monier's analysis, 17·8 per cent. ethylene and 71·9 per cent. "light hydrocarbon," i. e. methane—which seems very doubtful). Similar processes are indicated in the English patent of Hengst, Watson, Muschamp, and Wilson (1858), and that of MacCrachen, Newton, Kirkland and Husson. Still and Lane (Engl. patent, 6 Oct. 1871) mixed tar, together with some vegetable matters, with gas-coal. According to Bunte || all these endeavours led to nothing, as

* English Patent of 1854.

† Dingler's Journal, cxlviii. p. 292.

‡ Ibid. cxlviii. p. 295.

§ Ibid. clv. p. 462.

|| Schilling's Gasbeleuchtung, 3rd ed. p. 231.

those substances which by decomposing at a high temperature furnish permanent gases are present in coal-tar in too small a quantity. The rising value of tar makes all such attempts even less likely to succeed now than in the past.

Another obvious employment of tar, where it cannot be better utilized, is for *heating*, especially the retorts themselves. Its heating-value is calculated to equal once and a half or twice that of coke. Descriptions of apparatus suitable for this purpose are found in the 'Journal für Gasbeleuchtung,' 1859, No. 9, in the patents of Buchner *, of Cotton †, in Schilling's 'Handbuch der Gasbeleuchtung,' 3rd ed. p. 323, &c. &c. We shall describe similar apparatus in Chapter VII., when treating of the applications of dead oil.

Coal-tar was always extensively employed for the *preservation of building-materials* of all kinds. Stones as well as iron and wood can be preserved much longer, and protected against atmospheric influences, by a coating of coal-tar.

For *stones, brickwork, &c.*, especially when exposed to the action of acid vapours, Kuhlmann ‡ strongly recommends painting with coal-tar. Long before that, it was usual in chemical works to boil the stones intended for erecting acid-tanks, hydrochloric-acid-condensers, chlorine-stills, &c. in gas-tar somewhat boiled down, also to paint the brickwork of the furnaces and any wood or iron work exposed to acid vapours with coal-tar, nay, even to soak the roofing-tiles in the same; and this is done up to this day. It has been noticed at the works that coal-tar not merely renders those objects less liable to be acted upon by damp, acids, &c., but makes the stones much harder and able to resist mechanical wear and tear. Hence the stones intended to be used for acid-cisterns and the like must be completely dressed by the stone-masons before they are put in the tar-pan, because they will not take the chisel after boiling. Fireclay pipes, which in the crude state are not even watertight and are extremely fragile, after boiling in tar turn acid-proof, hard, and very little sensitive to changes of temperature. But there is no reason why the employment of coal-tar in this direction should be confined to chemical works. It has been observed that brick paving lasts very much

* Wagner's Jahresb. 1867, p. 758.

† English patent of Nov. 22, 1872.

‡ Compt. Rend. lvi. pp. 1069, 1146.

longer if the bricks have been first soaked in hot tar. This is equally the case with roofing-tiles, and is as good as, though very much cheaper than, glazing them, to make them stand the weather. For all these purposes the tar should be deprived of water and of its most volatile oils by evaporation or (much more rationally) by heating in a still; and much the best is the varnish made from pitch and tar-oil (compare Chapter V.).

Tar is also employed for *painting metals*. When laid on hot, as frequently practised by blacksmiths, it produces a shining and lasting black coat. Also cast-iron gas-pipes are mostly protected against rusting by a coat of tar laid on hot. That this is regularly practised in chemical works, has already been said. In such cases it does not matter that such a coat is rather rough and thick. If, however, a thin, equal, shining and lasting coat is required, in the place of raw tar one of the varnishes made from pitch and tar-oils, which are described in Chapter V., must be employed.

For *preserving wood* coal-tar was recommended as early as 1799, by Le Bon; but for this purpose it is inferior to wood-tar, which even now is exclusively employed in ship-building. Wood-tar penetrates much more deeply into the pores of wood, covers it with a coherent coat; and the preservative action of its phenols is assisted by its paraffine. The drawbacks of coal-tar are its free carbon and its naphthalene. The former prevents the tar from entering the very finest pores; the latter, volatilizing even at ordinary temperatures, leaves rents in the coat. Some go so far as to say that coal-tar produces interior rotting of the wood; but this has not been positively proved, and the manifold employment of coal-tar in chemical works has never led to such a result. At all events the tar-varnishes are preferable to crude coal-tar for wood-painting also. *Tar-vapours* are said to act even better than tar in preserving the wood; this has been patented by Robbins in the United States, by Paradis in Austria*.

Rives† recommends as a substitute for wood-tar a mixture of coal-tar, rosin, and lime. A mixture called *sulphur-tar* or *benz-asphalt*, prepared by boiling 2 parts of sulphur with 3 parts of coal-tar, has been strongly recommended as protecting wood, iron, and stone against decay and rust. A similar mixture is the *wood-cement*, employed as a roof-covering (Chapter V.). A mixture of

* Wagner's Jahresh. 1871, p. 848.

† Dingler's Journal, clvii. p. 317.

coal-tar with its own weight of hydraulic lime, Portland cement, &c. is said to liquefy at 70° , and to yield on cooling a soft, pliable varnish, resisting acids and specially adapted for wood under water, water-pipes, and roofing-tiles*.

Coal-tar plays an important part in the manufacture of *roofing-felt*, which is extensively employed (more so on the Continent than in England) for covering factories, agricultural buildings, &c. The manufacture is very simple, if suitable sheets of millboard or felt be provided. These are either boiled in completely dehydrated tar, or continuously drawn through hot tar, the excess being squeezed out by rollers, which at the same time causes the tar to penetrate into the interior of the felt. Since the tar in being dehydrated loses some of its valuable oils, this operation should never be performed (as it used to be) in open pans, but in stills heated by steam, so that the naphtha can be condensed. It is cheaper and probably better to employ "prepared tar," i. e. a mixture of coal-tar pitch with heavy tar-oil, freed from anthracene and phenol (Chapter V.). Roofs made with this material must be repeatedly painted with a similar mixture, especially during the first years, and always covered in between with a thin layer of sand, if they are to keep well.

Even in 1868, of the 9000 tons of tar produced at the Berlin gas-works, only one sixth part was distilled; five sixths were worked up for roofing-felt. It is different now.

The *antiseptic* property of coal-tar has for a long time been known and made use of; its action as a paint on wood depends partly upon this. No doubt it results from the fact that tar kills the lower organisms. For this reason it has also been tried against the potato- and grape-disease; but in these cases the cure may be worse than the evil. Tar, or mixtures containing it, is frequently used for disinfecting cesspools, sewers, &c. The best-known in England is MacDougal's disinfecting powder, in Germany Stüvern's disinfecting mixture (100 slaked lime, 15 coal-tar, 15 magnesium chloride). No doubt raw tar is inferior in this respect to the specifically disinfecting substances it contains, such as phenol and naphthalene.

As one of its direct employments the combustion of coal-tar for the purpose of manufacturing *lamp-black* may be classed; but it is not so well adapted for this purpose as the heavy oil distilled from

* Dreyssig, German patent 10,685, Oct. 13, 1879.

it. According to Newton's patent of 1854, lampblack can be obtained directly by mixing 160 lb. of coal-tar with 200 lb. of slaked lime, adding 18 lb. of alum, and strongly heating the well-kneaded mixture without access of air in fireclay crucibles or iron cylinders, as in preparing bone-charcoal. The product has to be allowed to cool down without access of air, and is at last finely ground. By altering the proportions of tar and lime, all shades between brown and grey can be obtained.

The following exact description of lampblack-making has been given by Nepp*. The tar is employed for heating six steam-boilers, 13 feet long, 2 feet 2 inches in diameter, which jointly supply an eight-horse-power steam-engine. The tar is run into tanks holding two barrels each, one in front of each boiler. Behind the boiler is an oven, in which the gases from the burning tar, which have been partially cooled in their way through the boiler-flues, deposit the soot contained in them upon horizontal and vertical shelves, which divide the oven into several compartments. The lightest particles of soot are deposited in the highest part of the oven; and this does not require to be so often emptied as the middle and lower shelves, which contain most of the lampblack and are emptied directly after the tar has been burnt off. The work lasts six hours by turns, three ovens always going together, so that there is always enough steam. In the fireplace a residue of fine coke is found. The ovens are well bound and covered with metal plates. They are 13 feet high; the upper 3 feet project through the roof, so that they are cooled from without. They are accessible from below by an iron door, from above by iron steps. The lampblack is partly left as it is; but most of it is mixed with peat, finely ground under edge-rollers, and sifted before it is sent out. The steam generated in the boilers is employed for driving a peat-mill, manufacturing the casks, &c. The cost of plant is about £400 to £450. The product serves for manufacturing colours, shoe-blackening, black-lead for stoves, &c.

Thenius† describes several lampblack-furnaces of a very simple kind, intended for burning tar-oils, pitch, &c. The furnace for "soot-oil" consists of a metal plate kept red hot from below by a local small fire; it forms the bottom of a brick chamber. Upon this the "soot-oil" constantly drops in a fine stream from a tank,

* Chemiker-Zeitung, 1878, p. 222.

† Die technische Verwendung des Steinkohlentheers, p. 132.

whilst a side door with small holes admits the air necessary for combustion. The smoke enters four brick chambers communicating with a chimney. When the oil intended for combustion has been used up, the furnace is left standing for a few days, and the four chambers are opened by doors provided for the purpose. The last chamber (next to the chimney) contains the finest lampblack (for lithographers); the third one the next finest (for printers); the second and third contain coarser soot, which is well sifted and sold as common lampblack. The best kind is sometimes further refined (for paper-makers, colour-manufacturers, lithographers) by ignition in sheet-iron cases whose covers are luted with clay. They must be heated for some time in a furnace with a good draught, till all empyreumatic oils have been driven off and the soot remains behind without any smell. The cases must be left to cool for several days before opening them, because the soot cools very slowly and would take fire if it were exposed to the air too soon. This is "half-calcined lampblack;" the "thoroughly calcined" article is obtained by igniting the first product once more in fresh cases and treating it as above. 400 lb. of "soot-oil" (*i. e.* heavy coal-tar oil) are to yield 20 lb. finest lampblack, 30 lb. seconds, and 20 lb. of the third and fourth qualities. On the metal plates some coke remains, which is knocked off and sold as fuel.

J. Brönnert* burns all waste products of tar-distilling under a specially constructed steam-boiler of somewhat complicated construction, and forces the products of combustion by means of a fan-blast of 7 feet diameter through long flues, provided with ground-in bottom-slides, into a soot-chamber. The slides serve to admit air as well, in order to make different qualities of soot, according to their position, for all technical purposes—such as "fat soot" for oil-cloth manufacturers, and calcined soot of all kinds for patent leather, india-rubber, and printers'-ink manufacturers.

Wilhelm and Bohnstadt† make *printers' ink* by mixing 100 parts of coal-tar with 6 to 15 rosin and 10 paraffin oil, forcing through a sieve, treating with bleaching-powder to destroy the smell, and mixing with 20 to 25 parts of glycerin and 12 to 18 parts of lampblack; for the finer qualities a dark aniline colour is

* Private communication.

† German patents 12,282 (Dec. 25, 1879) and 12,286 (Jan. 6, 1880).

added. Or the tar is first heated with $2\frac{1}{2}$ or 3 per cent. sulphuric acid, neutralized with soda, treated with chlorine as above, mixed with $2\frac{1}{2}$ or 3 parts of lard and 4 or 5 parts of glycerin or 8 to 10 parts of soap. Sometimes they add $\frac{1}{10}$ to $\frac{2}{10}$ per cent. lampblack and log-wood extract with bichromate of potash, alum, or cream of tartar.

For making *patent fuel* (briquettes), coal-tar was formerly used, but has now been universally replaced by pitch, as will be explained in Chapter V.

CHAPTER IV.

THE FIRST DISTILLATION OF COAL-TAR.

It has been mentioned more than once in the preceding chapters that the utilization of tar by distillation is a comparatively new industry ; but it had long been known that useful products could be obtained by that operation. In this respect a patent awarded to Henry Haskins, August 7th, 1746, *i. e.* half a century before the first introduction of gas-lighting, is so remarkable that I quote it verbatim, as follows :—

“ New method of extracting a spirit or oil out of tar, and by the same process produce the finest of pitch.

“ First, take any quantity of tar you please, so as not to more than half fill your still, which must be thoroughly cleaned from all manner of impurities, and more particularly from water ; for if any quantity of that should be left in it, it will be found to be exceeding troublesome and considerably hinder the operation.

“ The tar may be cleansed either by boiling or straining, or by settling in tubs, or any other convenient vessel ; then commit it to a double-neck pelican-headed still, made either of glass, iron, or copper, with capacious receivers and well luted, under which raise a fire of the first degree for six hours, by which time the particles will be thoroughly comminuted ; then raise your fire to the second degree for as many hours more, and then to the third degree for three hours more, in which time you will find first a pale acid phlegm to come off into the receiver, which must be changed, when a fetid volatile oil or spirit rises ; lastly will come over a black glutinous oil, which keep for use.

“ If you would have a more volatile or light oil, which may be

more proper for many uses in physic, it may be done by many repeated rectifications to what degree you choose.

“Lastly, the caput mortuum, which is what remains in the still after the distillation is finished, will be found the finest and best of pitch, which I am well assured of, not only from my own judgment, but by the experience and testimony of many who have used it.”

It is quite possible that in this patent wood-tar is meant, which at that time was much better known than coal-tar; but the principles of the distillation of the latter appear quite clearly in that old patent.

Carriage of Coal-tar.

Very different descriptions of vessels are used for carrying the tar from the gas-works to the distilleries, according to the circumstances of the case. In England water carriage is preferred wherever it is practicable, the canal-boats being constructed as floating tanks, with a cabin for the crew, which serves also as an air-space for augmenting the carrying-power. Such boats hold as much as 10,000 gallons or about 50 tons of tar. On the continent this is rarely possible; there the tar is usually carried by railway, in cylindrical or angular iron tanks fixed on a platform running on wheels. If these tanks are made of pretty strong iron, they can be steamed out whenever the tar has become too thick, which may happen in winter. Angular (box-shaped) receivers are more easily got at and cleaned inside; they hold about 10 tons, a truck with two cylinders about 9 tons of tar.

In Paris (and elsewhere) tar is carried in iron or wooden casks resting on axles and drawn by horses, or, wherever possible, laid on railway trucks. In Lancashire* it is usual to employ wooden barrels (preferably of ash-wood), holding from 250 to 300 gallons, resting by means of concave wooden bearers upon two-wheeled carts. The middle bearer rests just over the axle; and the barrel can be tipped behind, two iron adjustments attached to the back bearer preventing it from slipping down. There is a running-off cock of 2- or 2½-inch bore, and a charging-hole 4 or 5 inches square and closed by a wooden plug. Long barrels are said to be pulled more easily than those more bellied. A barrel costs about £3, the cart belonging to it £14.

From the canal-boats or trucks the tar is frequently pumped

* Watson Smith.

by steam-pumps into iron *store-tanks*, situated high enough for the tar, after the water has separated, to be run into the stills by natural fall. In Paris the draw-off cocks of the four cylindrical iron store-tanks, which rest on high pillars, unite into a common main, which descends to the ground, runs under ground along the whole set of tar-stills, and gives off an upright supply-pipe with slide-valve for each still, by which these can be filled as required, by means of the hydrostatic pressure from the store-cylinders. In other cases the tar, especially when it arrives in casks, is emptied into larger store-cisterns sunk in the ground, and pumped from these either into the above-mentioned high tanks, or directly into the stills.

Such underground tar-wells (as well as those for ammoniacal liquor) are frequently of very large dimensions*, as tar-distillers are generally bound by contract to rid the gas-works of their tar and ammoniacal liquor, which in the case of stoppages of business, accidents to the plant, &c., might cause them considerable embarrassment. On the other hand, if there is large storage room, a good stock may be collected in winter, when the gas-works are busiest, so that even in summer the stills can be regularly employed (Watson Smith).

Underground wells are not often made of iron, this being too costly and subject to corrosion. Usually they are made of brickwork set in cement, of a circular shape, secured underneath and round the sides by clay puddle. First the necessary excavation is made; then a good puddle is laid down on the bottom, completely levelled, and a double floor of bricks in cement laid on, the joints crossing each other. Now the sides are raised, likewise in double courses and hence 9 inches thick, leaving between the brickwork and the soil (in case of need kept back by wooden stays) a space of 8 or 12 inches, which is filled in with puddled clay. The best method of proceeding is to complete each time a ring of about four feet height, puddle behind it, and continue the walling. It is best not to work too fast, so that the brickwork may have time to settle; cracks once formed can hardly ever be repaired (Watson Smith).

The tar-wells are often tightly covered with planks, to keep off the rain &c. At the place where the carts are tipped there is a strainer with many $\frac{1}{2}$ -inch holes and with sides and back, so that

* Watson Smith mentions some of 60 feet diameter.

any bits of wood which might choke the pumps are kept back (Watson Smith). Or else all the carts discharge their contents into a large spout, provided with outlets for each cistern (if there are several).

The *pumping* of tar is nearly always done by ordinary donkey-pumps. Raising by compressed air, which is otherwise so much employed in this industry, does not answer so well for the tar itself. The suction pipe is perforated at the bottom with a number of holes, or is surrounded by a strainer, in order to prevent choking up by chips of wood or the like.

DISTILLATION BY STEAM.

The manufacture of coal-tar products begins by fractionally distilling the tar, mostly by a naked fire, but in some places or for special purposes by means of *steam*. The latter plan is now very little used at large works—except in Scotland, where it appears to be general. Its advantage is only apparent where the tar has merely to be dehydrated and deprived of its most volatile constituents in order to employ the remainder (95 per cent.) for painting, for impregnating stones or roofing-tiles, or for the manufacture of roofing-felt (compare p. 80). In such cases much trouble and danger of fire is avoided by substituting steam for a naked fire. The steam can be applied indirectly, as “dry steam,” by surrounding the still with a jacket, or by means of a coil in which the steam circulates inside the vessel and issues again to the outside. In the outlet it is expedient to fix an apparatus for automatically discharging the condensed water, without allowing any steam to escape, of which apparatus many kinds are made now. The still may be almost of any shape; perhaps the best is an upright cylinder. The escaping vapours are condensed in a leaden or iron worm, and separate in the receiver into ammonia-water and light oil, which is mostly sent to the larger tar-distillers for rectification.

Perhaps it is more usual to employ “wet” steam, directly blown into the still, *e.g.* by means of a coil of pipes lying on the bottom and perforated with many holes. According to Ure such stills hold from 800 to 1500 gallons, and the distillation is carried on till the specific gravity of the distillate has reached 0.910. According to Mills* the stills hold from 500 to 4000 gallons, and

* ‘Destructive Distillation,’ p. 23.

are horizontal cylinders; the steam brings over about 10 per cent. at most of light naphtha (sp. gr. 0·78–0·83) and some ammoniacal liquor. The residue is run into cisterns, where, on its settling, tar and water separate. The “boiled tar” is now ready for the above-mentioned purposes, or can be run while hot into other stills for distilling by naked fire. But the latter is not advantageous, because there remains very much water with the tar, which can only be separated from it by long rest; hence, if a naked fire is to be used, it is best to do so from the first.

The condensation of the escaping steam and naphtha-vapour, owing to the large quantity of the former, is rather more troublesome than when the distillation is effected with “dry” steam or with a fire. There is much more cooling needed, *i.e.* longer worms and more cooling-water. The condensing mixture of naphtha and water divides at once into these two constituents, which can be kept apart by overflow vessels, as will be mentioned hereafter in describing the rectification by steam of the lightest oils (Chapter X.).

The usual yield of naphtha by this plan is 2 to 6 per cent. from ordinary tar, or 10 to 20 per cent. from cannel-coal tar. The longer the operation is continued, the more, but the heavier, naphtha is obtained.

The *naphtha* obtained by steam distillation is of course richer in volatile constituents than that obtained by direct distillation of tar. But it is far from containing only such constituents as boil at and below the temperature of the blown-in steam (rarely above 150°); a quantity of much higher-boiling substances are carried along, as shown by the following analyses * :—

	I.	II.	III.
Oils up to 100°	20·9	14·2	23·3 per cent.
„ 130°	5·9	13·2	8·0 „
„ 160°	8·7	19·6	15·2 „
„ 202°	16·0	16·6	23·9 „
Oils boiling above 202°			
(by difference) . .	48·5	36·4	29·6 „

		sp. gr.
I.	Naphtha from the tar of the Hamburg gas-works,	0·964
II.	„ „ „ Berlin English „	0·947
III.	„ „ „ „ Corporation „	0·932

* From Kerl-Stohmann's 'Chemie,' 3rd ed. vi. p. 1172.

Hence this product is nothing like so valuable as the "first runnings" of distillation over a naked fire, and is more similar to the "light oil" of that operation.

Instead of distilling by steam, in Scotland *, sometimes a fifth of its bulk of water is added to the tar and the whole distilled by a direct fire. Less, but better, naphtha than by steam distillation is said to be thus obtained. This process comes to the same thing as distilling by steam of ordinary atmospheric pressure, but does not seem recommendable, as the danger of boiling-over will be very great.

DISTILLATION BY FIRE.

The more usual way of distilling tar, by a direct fire, has for its primary object the removal of the non-volatile or too-little volatile constituents, which form the greater portion of tar, in the shape of pitch, and to effect a preliminary fractionation of the distillates, which are then worked up singly. It is evident that this can be done only by a direct fire, since the boiling-point of the most valuable product from tar, anthracene, coincides with that of mercury (360°).

Dehydration of the Tar.

It is the first condition of a quiet regular distillation that the tar should be freed as much as possible from the ammoniacal liquor which is always mixed with it to a certain extent, and whose presence is a disturbing element in the distillation. So long as water and tar-oils boil at the same time, there is always a tendency of the liquid to "bump," or even to be jerked over explosively. This can be overcome by very cautious, slow firing; and shortening this stage of the work is decidedly desirable, although it is hardly possible to do without it altogether. Hence *previous dehydration* of the tar is decidedly advisable whenever it can be done without too much trouble.

If the tar be sufficiently fluid, mere prolonged rest will separate a large portion of the ammoniacal water from it; for as the water is only mechanically suspended in the tar and is of less specific gravity, it will rise to the surface, whence it can be drawn or ladled

* Ronald and Richardson, 'Chemical Technology,' vol. i. p. 733; Mills, loc. cit. p. 23.

off. In many places nothing else is done for this purpose but storing the tar in several large cisterns, which are best placed at such an elevation that the tar can be run from them straight into the stills. Whilst one of these cisterns is being filled by pumping in fresh tar, the others are allowed to rest; and from that which has stood longest the now somewhat dehydrated tar is drawn off*. At some of the best works a closed steam-coil is laid in those cisterns, by means of which the tar can be heated at will, in order to make it more fluid, and to separate the water better. In summer there is no occasion for this; but in the colder seasons the tar is heated, in Paris to 16° or 17°, in London to 20° or 21°, in German works sometimes up to 40°.

According to Girard and Delaire †, the dehydration of tar is effected by heating to from 80° to 90° in large boilers, by means of a steam-coil or jacket, or by a direct fire. The volatilizing oils are condensed. After from 20 to 30 hours the separation of tar and water is sufficiently complete, so that the water collecting at the bottom (?) of the boiler can be drawn off by a cock. The tar is now charged hot into the stills.

If this description were correct, it would come to the same thing as the process described on p. 87; only it is called a dehydration instead of a distillation as we have called it (assuredly more correctly). But we have already stated that a division of the distilling process into two phases, by steam and by direct fire, whether it be theoretically correct or not, does not seem to have stood the test of practical experience; for none of the largest works proceed in this manner. Girard and Delaire's description is evidently at fault in that it makes the water collect *below* the tar, which is impossible in the case of coal-tar. The same error is committed by Bolley ‡, undoubtedly from a confusion between coal-tar and browncoal-tar &c. In consequence of a similar inconceivable confusion, C. Vincent § states the specific gravity of *coal-tar* as 0·85 to 0·94!

Perhaps the most rational method of dehydrating the tar is the

* According to Watson Smith, at small works tar and gas-liquor are allowed to settle in the same tank; the tar is drawn off by a tap in the bottom, the ammoniacal liquor by one placed higher up, into their respective stills.

† *Dérivés de la Houille*, p. 7.

‡ *Chemische Technologie der Gespinnstfasern*, p. 27.

§ Payen's '*Précis de Chimie industrielle*,' 1878, ii. p. 944.

following, practised at one of the largest and best German tar-distilleries. The tar is pumped as it is into the (very large) stills, until it begins to run out of a small overflow-cock placed just below the upper dome of the still, when the pumping ceases and the firing is started. Before the tar arrives at the boiling-point, it has, of course, turned quite thin, and most of the water has collected on its surface. But as by the heating the bulk of the liquid is increased and its level rises above that of the overflow-cock, the watery portion can be drawn off by opening that cock from time to time. Even if a little tar should come along with the water, no harm is done. Whatever vapours are given off during this heating must pass on to the condensing-apparatus, and are thus utilized.

A peculiar dehydration-process has been proposed by Foucault *. The tar is to be distilled in a revolving still, whose contents are thus constantly agitated. Thus the evaporation of the water and of the oils accompanying it is said to go on without bumping and frothing up. This process does not seem very practicable.

Previous Purification of Coal-tar.

E. Jacobsen † proposes purifying the tar previous to its distillation. If coal-tar be mixed with half its volume of carbon bisulphide, all the free carbon will separate as a powder; and if the liquid be decanted, the carbon bisulphide blown off by steam, and the residue mixed with petroleum spirit, all the brown asphalt will be left behind, whilst the remaining liquid, the petroleum spirit having been steamed off, will consist of an orange-coloured clear oil containing naphthalene, anthracene, &c. Similarly coal-tar pitch can be purified from its carbonaceous and asphalty portions; the hydrocarbons remaining over are more easily fractionated; and less of them is gasified on heating, so that anthracene can be recovered from them with more facility. Carbon bisulphide and petroleum spirit are easily recovered without any essential loss (?). When petroleum spirit is added directly to coal-tar, the asphalt, which is precipitated, forms, with the free carbon and a portion of the dead oil, a tough, difficultly manageable mass; and by adding a mixture of carbon bisulphide and petroleum spirit, part of the brown asphalt

* Chemiker-Zeitung, 1880, p. 572.

† Chem. techn. Repertorium, 1869, ii. p. 107.

is dissolved. Hence the process should be carried out just as above described. The author is not aware that this process has ever been carried out on the large scale. It seems too expensive and too dangerous in respect of fire; and probably a good deal of anthracene will be left in the "free carbon" and the "brown asphalt." Neither would it be easy to obtain the benzol free from carbon bisulphide.

Construction of Tar-stills.

Only one material is suitable for tar-stills, viz. wrought iron. Cast-iron stills would be less exposed to burning away, and to mechanical injury in clearing them of coke; but they cannot be easily made of a considerable size. Both the difficulties and the cost of casting increase very rapidly with an increase of the size of hollow objects; neither can a perfect uniformity of structure be expected in the case of unusually large castings.

Even when they are made as upright loam-castings and with a large feeding-head, an air-bubble may very easily remain, and, in the case of vessels exposed to a direct fire, cause in that place a most dangerous tendency to crack. But even a faultless casting is still very much exposed to cracking, and must never be set without a curtain arch over the fire-place: and for all that, any carelessness of the fireman will cause it to crack; and the mischief will then be great in proportion to the size of the vessel. Wrought-iron vessels, on the other hand, cannot be cracked by incautious firing, at least not in consequence of sudden changes of temperature, although an explosion from an excess of pressure, if all outlets are stopped up, is still possible. It is true that the plates are more easily burnt by the first action of the fire than cast-iron; but this must, under any circumstances, be provided against by a curtain arch. It takes very gross and long-continued carelessness on the part of a fireman to burn the plates of a properly set still, whilst even the best workman cannot always help the cracking of a cast-iron still.

It should be further noticed that the metal of cast-iron stills must be at least four times as thick as the usual boiler-plates; this makes the former much more expensive than the latter, and increases the consumption of fuel. Lastly, wrought-iron stills can be repaired by patching, or by putting in fresh plates, whilst similar repairs are nearly always excluded in the case of cast-iron.

If wrought-iron stills are protected, by means of a curtain arch, from injury by the first heat of the fire, they last very long, provided they are properly treated, especially in cleaning out. A new still should go at least four years without any great repairs, and as long again after each thorough repair. The plates burn through most easily at the bottom, where the flame issues from underneath the curtain arch, if the latter does not reach right through. Where this is the case, so that the still-bottom is not touched at all by the flame, and is only as it were in a hot-air bath, the stills may last much longer than the above-mentioned time.

The following general rules should be observed in constructing the stills. The *thickness of the plate* as a rule need not be over $\frac{3}{8}$ inch; the very greatest, for 40 or 50 tons of tar, should be $\frac{1}{2}$ inch. Of course the plates must be very well riveted and caulked; but in spite of that the seams of new stills often show a tendency to leaking at the end of the distillation, when the temperature has risen very high. This is seen by a flame running along the seams or rivets; it always occurs at the bottom, and can be cured by fresh caulking. Even without that, coke soon sets into the seams and makes them light; hence such leaking is mostly noticed after a thorough cleaning of the stills. In any case it does not endanger the safety of the still. The same thing holds good of the stills for light oil and other similar ones, to be mentioned hereafter.

Much difference of opinion exists as to the best *shape of a tar-still*. Formerly any thing was made to do, especially old steam-boilers of various shapes. Mostly this was bad economy; increased consumption of fuel, longer time of working off, frequent repairs, and frothing over of the contents of the still amounted to several times the cost of a new tar-still of the best pattern. But there is much dissension upon the point, what is the best pattern for a tar-still? The following is a description of the various forms of stills found by the author in 1880 at well-conducted works in different countries.

That shape of still which is met with almost universally in England, and which the author has seen at the majority of German works also, is an *upright cylinder*, of nearly equal height and diameter, with a dome-shaped top and a concave bottom, *i. e.* equally curved upwards in a dome-shape. This concave bottom is preferable to a flat bottom, on account of its greater stiffness

and larger heating-surface, and because the iron can better expand and contract with the inevitable great changes of temperature to which it is exposed. Convex bottoms would have equal advantages, but would not present such a favourable proportion between the heating-surface and the contents of the boiler as concave ones, they are not so easily set, and the pitch could not very well be run out completely by means of a cock in the deepest part.

Such stills are always made of considerable size, both to save labour for attendance and because the separation of the products according to their boiling-points is easier the larger the quantity treated in each operation. Rarely are smaller stills used than those for a 6-ton charge; but they are sometimes preferred, because a charge can be worked off in 10 or 12 hours, and night work thus becomes unnecessary. But the large works usually have larger stills:—in England, holding from 10 to 20 tons, rarely more; in Germany, 20, 25, or even 50 tons. It is doubtful whether such very large stills are the best; 20 tons seems the most convenient size.

Watson Smith advises trying the tightness of each still by putting it on its seat, connecting it with a steam-boiler, closing all openings, and blowing in steam at $2\frac{1}{2}$ atmospheres' pressure; it should not leak anywhere then. (Evidently an air-cock must be left open till all the air has been expelled.) He also observes that there is usually some difficulty in fixing the cast-iron still-head, inasmuch as the cover is mostly made of several pieces overlapping each other at the seams, and thus presenting obstacles to a tight joint with the flange of the still-head. This can be avoided, either by making the top piece out of one plate, with a circular opening for the head, or else, if the top is constructed of several pieces, by making a wrought-iron ring fitting the central opening (previously provided with rivet-holes), hammering it down while red-hot, so that it adapts itself to all the uneven places of the joints, marking the places for the rivets, taking the ring off, punching the rivet-holes, putting the ring on again, and riveting it fast to the top. The inner border of this ring, projecting into the central opening and left quite smooth, serves for bolting on the still-head.

The usual *cement* for tar-stills is the ordinary rust-cement, made of iron borings, sal-ammoniac, and sulphur, moistened with a little

ammoniacal liquor. Watson Smith recommends a cement made of 2 parts iron borings, 2 sifted quicklime, $1\frac{1}{2}$ common salt, $\frac{1}{2}$ flowers of sulphur, well mixed up and made into a paste with ammoniacal liquor. When it has set and has been exposed to the heat of the still, it turns very hard and resists the fire very well.—Instead of any cement, it seems preferable, wherever possible, to employ asbestos packing, which is well-nigh indestructible, but rather porous, if employed in thick plates.

Some works employ a very different shape of still, viz. *horizontal cylinders* similar to steam-boilers. They are of course less in diameter (rarely above 7 feet), but longer, than upright stills. It would seem that they require more fuel than the latter form of stills, and that the tar has much more tendency to froth over in them during the first period of the distillation. The author has seen such horizontal stills, holding 18 tons, working very satisfactorily; but, on the whole, the upright form is evidently preferred.

Stills of a very peculiar shape are employed at the Paris gas-works. They are *waggon-shaped*, with an incurved bottom, and edges very much rounded (fig. 3), holding only 1440 gallons

Fig. 3.



of tar. The flues run twice round the sides of the stills. This shape, it was stated to the author, is preferred because it causes the least injury to the metal in contracting and expanding with

the changes of temperature. But such injury has not been observed where the usual upright cylindrical stills are at work; and the Paris shape has from the first the disadvantage of requiring two running-off cocks, one for each side (at *a a*). These stills are set so that the bottom is not touched at all by the fire, which circulates twice round the sides. In the lower flue the flame does not impinge directly upon the metal, which is protected by thin fire-bricks; in the upper flues these are wanting. Everywhere else the author has found the flame (which has expended its greatest heat upon the curtain arch beneath the still-bottom) heating the sides of the still without any fire-brick lining, and without doing any injury to the still. The stills at those works do not show the arrangements mentioned by Girard and Delaire* and by Wurtz†, by which as soon as the level of the tar sinks too low the upper flue is shut off and the fire is only allowed to circulate in the lower flue. But anyhow the flues heat only the lower part of the still; so that such a complicated arrangement is not called for. Even the upper flue is built in such a way that the level of the pitch at the end of the distillation is still above it—which is not very difficult to do, since the bulk of the pitch is at least half of that of the tar.

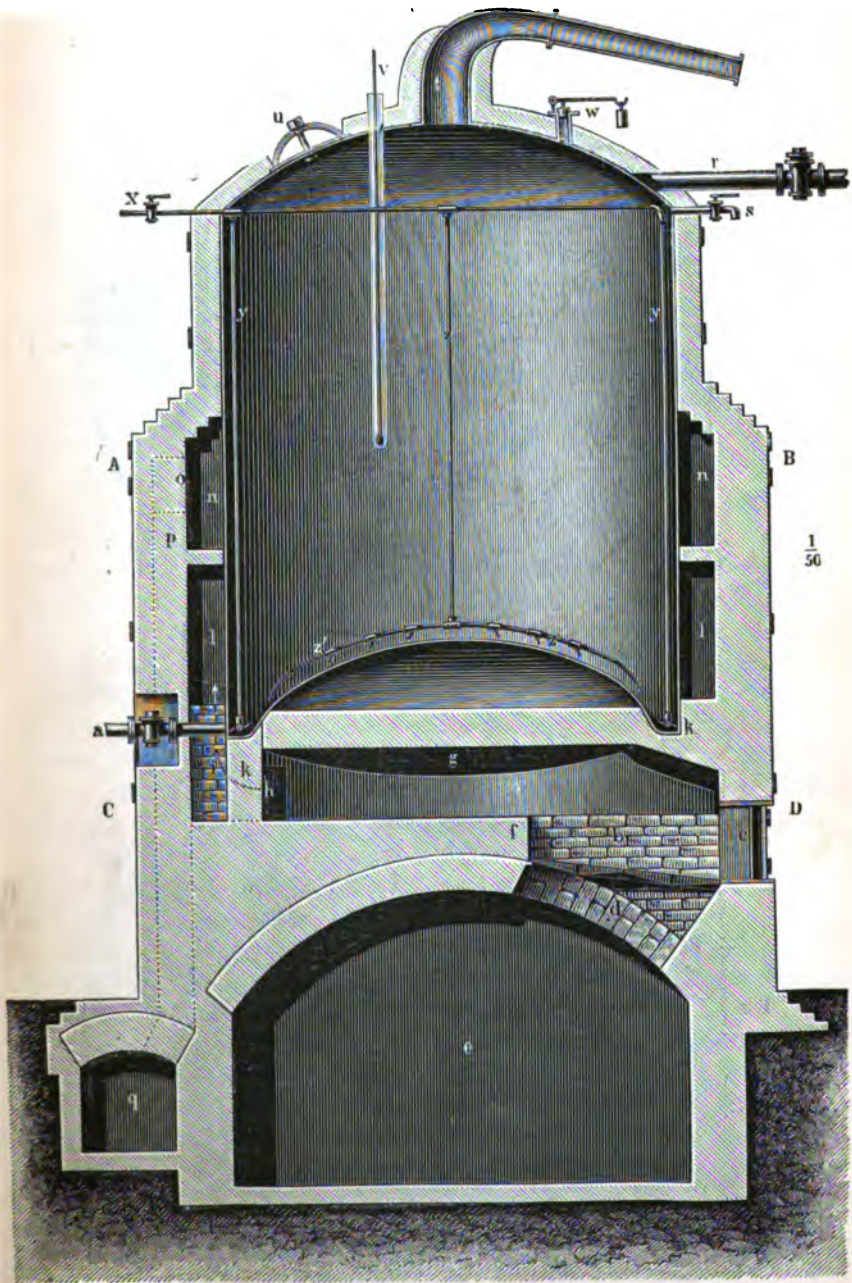
The various parts belonging to a tar-still are best described along with an explanation of the figures 4 to 6. These represent a *25-ton still*, the details of which, as well as those of the setting, are not copied from a particular plant existing at a factory, but combine those features of all the apparatus observed by the author in England and Germany which seem to him most practical. But each single part, described or drawn here or hereafter, is actually in use at one or another of the largest and best works.

Fig. 4 is a cross section along the line *E F* of the plans; fig. 5, a plan laid through *CD* of fig. 4; fig. 6, a plan of the still itself, along the line *A B* of fig. 4,—each $\frac{1}{50}$ of the natural size. The still is 9 ft. 10 in. wide, and 11 ft. 6 in. high (without the dome), made of $\frac{3}{8}$ -inch boiler-plate. The inward curve of the bottom is about the same as the outward curve of the top. The still may be set with a slight slope towards the outlet-cock *a*, which in any case is placed as nearly as possible just above the bottom, or even in the flat part of it. This is absolutely necessary if hard pitch is made;

* Dérivés de la Houille, p. 8.

† Matières colorantes, p. 23.

Fig. 4.



CTH. 100 57 50 52 0 1 2 3 4 feet

Fig. 5.

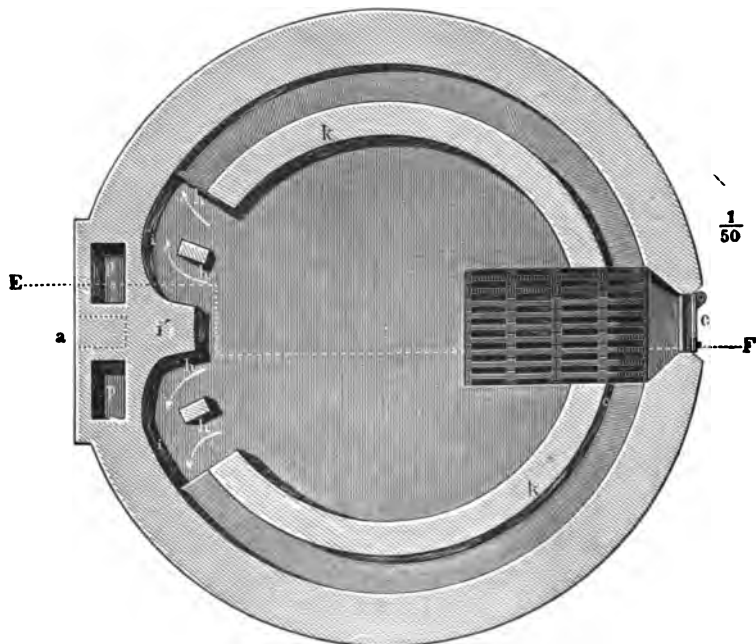
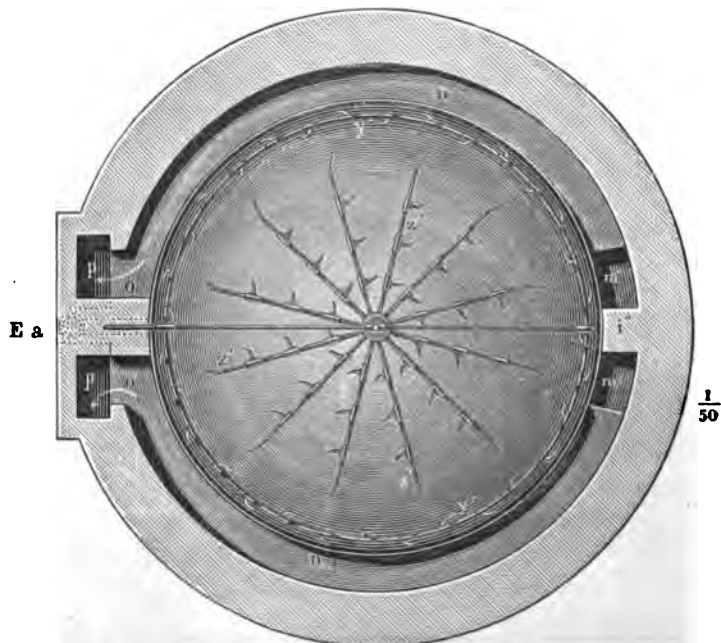


Fig. 6.



where only soft pitch is made, as is usual in Germany, it is not so essential.

The still is heated by a fire-grate, *b*, adapted to the special quality of the fuel. The usual fuel is small coal (slack); sometimes, especially at gas-works distilling their own tar, coke is employed, by which, however, the still-bottom may be injured unless completely protected by a curtain arch, or unless steam be introduced at the end of the operation. Sometimes, if the heavy oil is not easily saleable, it is employed for firing the tar-stills; we shall describe the arrangements for this purpose in the 7th Chapter.

The fireplace is accessible from without by a door, *c*. Where there are a number of stills, all the doors are arranged in the same lines, opposite to the side where the pitch-cocks *a* are placed. Usually the ash-pits under each grate communicate with the outer air by an opening below the fire-door. But in our diagrams is shown the arrangement at one of the largest English works. Here the ash-pits are closed below the fire-doors, and all of them communicate by an opening, *d*, with a large overarched passage, *e*, running along the whole set of stills and only accessible from the two extremities. This affords perfect security against fire in case of the tar boiling over and running out of the receivers. It is true that other precautions can be taken against this danger, such as constructing the receivers in the manner to be described below, where the tar, even if it boils over, cannot get at the still-fires. But the arrangement shown here will also act in the case of accidents to the pipes and, especially, to the still-head; for with it the vapours issuing in great force cannot take fire at the ash-pits. Moreover the underground passage *e* permits great cleanliness. It is useful to place a steam-pipe below each fire-grate, to increase the draught, to prevent overheating of the grate-bars and the fire-bars, and thus to avoid the formation of fluxed cinders.

The flame travels over the fire-bridge *f*, and under the arch *g*. This arch is sprung barrel-shaped from the annular wall *kk* on which the still is seated, and completely shuts off the still-bottom from the flame. Thus the space between *g* and the still-bottom is an air-bath, kept very hot by the flame below *g*, but never excessively so. So much heat is imparted to the arch *g*, that at the end of the operation no firing is needed, especially if steam or

exhaustion be applied. The weight of the still resting upon the annular wall *kk* enables this all the better to support the pressure of the curtain arch *g*, which is otherwise independent of the brickwork of the fireplace, and can be easily renewed when it is too much burnt out. The flame now travels on through four holes, *hh*, into two vertical flues, *ii*, and arrives at the cylindrical shell of the still. The solid pillar *i*, between the flues *ii*, is continued to the top. Through this pillar passes the pipe connecting the pitch-cock *a* with the still, protected from the fire, but kept warm by the flues *ii* and *pp*. The pillar *i'* forces the flame to divide into two currents, which pass round the lower part of the still in the annular flue *ll*, are prevented from uniting in front by the pillar *i''*, pass through the flues *mm* into the upper annular flue *nn*, return to the back part, and enter through *oo* into the downcast shafts, *pp*, communicating with the main flue, *g*. The shafts *pp* are provided in suitable places with dampers, by which equal heating of both sides of the still can be secured. For shallower stills a single annular flue would be sufficient; its downcast shafts would have to be arranged in front, at each side of the fireplace. The best width of the annular flue is from 9 to 12 inches.

The outer wall, as far as the flues reach, should be at least 14 inches thick, and should be strengthened by several iron bands, shown in fig. 4. Above the flues the still is surrounded by a 9-inch brick jacket to prevent cooling; the brickwork continues along the whole top, and preferably also up to the top of the still-head *t*. Such a protection against cooling is all the more needed if the tar-stills are under the open sky, or merely covered by a light corrugated iron roof, &c. This, the most usual style causes any explosions or fires to be less destructive than if the stills were placed in a substantial building. It is advisable in that case to protect the brickwork of the stills against rain by a coat of molten pitch.

In England the stills are mostly set in a simpler manner. The curtain arch reaches only as far as the fire-grate, or a little further; the flame impinges upon the bottom of the still, ascends at the back, travels in an annular flue round the still, and then goes away into the main flue (see fig. 7, p. 103).

The *mountings of the still* are as follows. A cast-iron *supply-pipe* *r* (fig. 4), closed by a slide-valve or in any other way, is provided for running-in the tar. It is best rather wide, say 6 inches,

so that much time may not be consumed in filling the still. Where the tar is not pumped, but run in from a high store-tank, a simple hole will do, afterwards closed by a screw-plug, or even the man-hole. There must be an *air-vent*, through which the depth of the tar can be gauged as well; but preferable is an *overflow-cock* *s*, of 1 inch bore. Through this, first air escapes; as soon as tar comes out of it the feeding is stopped and *s* is closed. Sometimes a special air-cock is present as well. We have seen on p. 91 that, during the heating up, the water collecting on the top of the tar can be removed from time to time by opening *s*, which greatly assists the work.

The cock *a* (fig. 4) serves for *running-off the pitch*; it will be described more exactly hereafter. Instead of connecting it, as is here shown, by a 4-inch pipe with the still, the latter is sometimes provided with a 12-inch pipe projecting through the brickwork, and in this the cock *a* is fixed. If the setting is similar to that shown here, the pipe is always hot enough for the pitch to remain liquid. But it is possible to work altogether without a cock, by forcing up the pitch through a vertical delivery pipe by means of steam (compare below).

The vapours are conducted away by the cast-iron *still-head* *t*, which decreases in width from 12 inches down to 6 inches, and is then continued into a 6-inch metal pipe leading to the condensing-tank. Sometimes a gutter is provided inside the still-head, at its base, to conduct directly outwards any liquid condensing in the rising part of the head, so that it cannot drop back into the still, where it might cause frothing up; but this is hardly necessary if that part of the still-head be surrounded by a bad conductor of heat. In some places they put a steam-pipe into the still-head, in order to remove obstructions by blowing through it. But a still-head of such a width cannot very well become obstructed, if it has a little fall. As to the connexion of the still-head with the still-top, we have described it on p. 94.

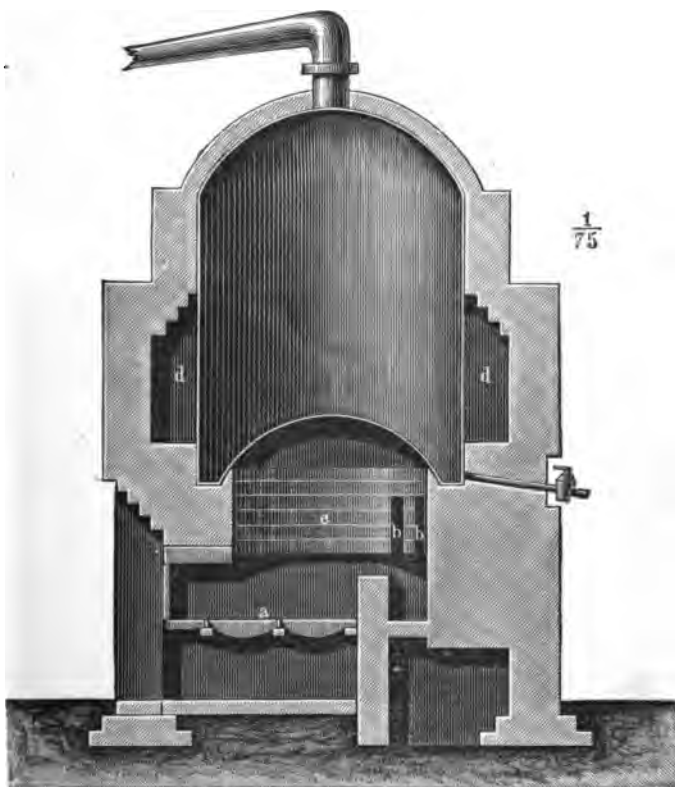
Every tar-still must have a *man-hole*. We have represented this at *u* (fig. 4), like a steam-boiler man-hole, closed by a cover fixed on by an arm and screw-bolt; the joint can be made good by plastic clay, or else by a ring of asbestos packing. But in some places the manhole-lid is made to serve at the same time as a *safety-valve*. It is then a plate, loosely laid upon a riveted neck, and joined to it merely by some cement which does not

become too hard. If the pressure within the still should for some reason or another mount too high, the lid will be thrown off before any other damage can occur. Unless some such contrivance is provided, there should be a proper safety-valve present, as delineated here at *w*; but many tar-stills are found without such. A very useful precaution consists in providing a side branch to the still-head, with a safety-valve opening downwards, which permits any tar that boils over to run to some safe place away from the still. Lastly, a *thermometer*, *v*, should be placed in an iron tube closed at the bottom and filled with iron filings or mercury; it should reach halfway down the still. In lieu of this, some works have pyrometers of various constructions, mostly not very reliable in their indications. Unless steam be applied in the last stage of the process, a mercurial thermometer cannot be used, since mercury boils at 360° ; in that case it must first be taken out of the iron tube. It should not be forgotten that mercurial thermometers which have been exposed to a high temperature for some time vary their fixed points considerably, owing to deformation of their bulbs; such variations have been observed to extend to as much as 14 degrees. Hence they must be compared with a standard thermometer from time to time; otherwise mistakes in the working and disputes with buyers may occur. This of course holds good of all thermometers used at tar-distilleries.

The reader will notice in our diagram (fig. 4) a system of *steam pipes*, *x y z*. We shall see afterwards that the majority of works now employ steam, mostly superheated, for finishing the process. This is usually done by means of a cross-shaped tube with perforations for the issue of the steam. Here we have shown the more perfect arrangement patented by Trewby and Fenner (No. 3613, Sept. 9th, 1879). The steam is introduced by a 1-inch pipe with tap *x*, which sends down three vertical branches *y z y* inside the still. The tubes *y y* communicate with an annular-shaped tube *y'*, placed in the lowest part of the still, and *z* with a system of branch pipes *z' z'*, covering the whole still-bottom. Both *y'* and *zz'* are provided with a large number of open, slightly bent outlet pipes with contracted ends. Thus the steam is divided into many thin jets, ranging all over the bottom of the still, which prevent its overheating and carry away the vapours of the heavy hydrocarbons. Owing to the large surface of the steam-tubes, the steam is superheated before issuing, and a special superheater is unnecessary.

One of the usual ways of setting tar-stills in England is shown in fig. 7*. Here there is no curtain arch at all; the fire of the grate *a* passes through the holes *b* in the annular wall *c*, and once round the still in the flue *d*. Sometimes the annular wall which

Fig. 7.



supports the still is strengthened by iron bearers, which probably do not last very long.

Condensing-Apparatus.

We append the description of these to that of the tar-stills. Girard and De Laire (*loc. cit.* pp. 8 and 10) state that sometimes a

* From 'Chemistry Applied to the Arts and Manufactures,' by Wm. Mackenzie, vol. i. p. 499. The other figures found in the same place, taken from Bolley's 'Technologie der Gespinnstfasern' (p. 210 *et seq.*) do not refer to the distillation of coal-tar, but of browncoal-tar.

still is provided with three condensing-worms, each regulated by a stop-cock, and employed one after another for the different fractions. None of the works known to the author employ that kind of apparatus, the object of which is not very clear, since the separation of the fractions need not commence in the worms, but can take place in the receivers. The author has never observed more than one condensing-worm; but these are of a very different description. The English works mostly employ cast-iron pipes, in lengths of 9 and 6 feet, from 4 to 6 inches wide, and connected by elbow-pieces (figs. 8 and 9). The whole is contained in a wrought-iron tank, and is supported by strong iron stays (not

Fig. 8.

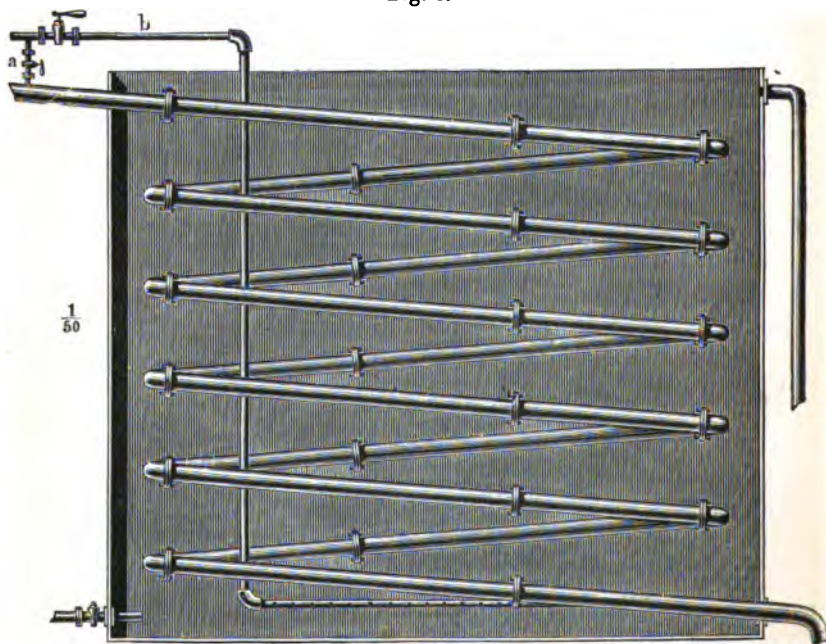
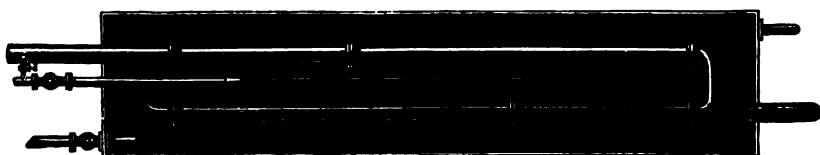


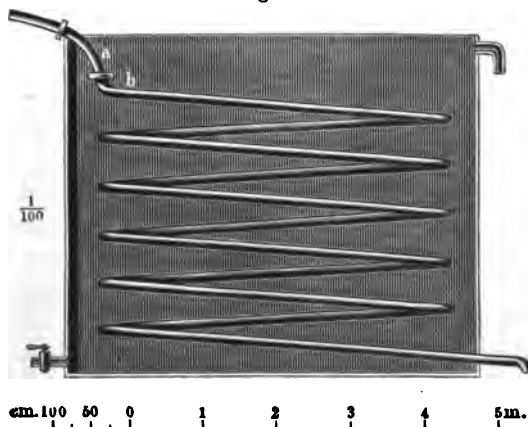
Fig. 9.



shown in the diagram). As the tank would be rather narrow, sometimes two worms, belonging to different stills, are placed in the same tank. Formerly the elbows were sometimes provided with cleaning-out holes; but these are quite unnecessary, if the pipes have enough fall and if the tank at the end of the process is kept warm. But it is always advisable to put a steam-pipe *a* in the top pipe, so that the worm can be purified by blowing steam through it in case of need. In any case there should be a steam-pipe (*b*) for heating the water surrounding the worm.

The German works prefer worms made of wrought iron or even of lead. In the latter case the cast-iron pipe *a* coming from the still (fig. 10) must be continued at least a foot below the level of

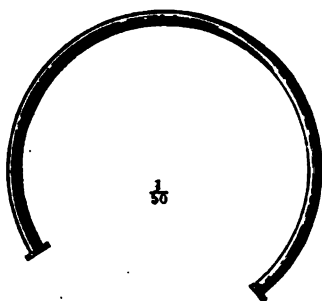
Fig. 10.



the cooling-water, and the lead-pipe *b* commence there; otherwise the latter might easily be melted at the end of the process by the heat of the vapours in the part not cooled by the water.

The majority of German works prefer drawn wrought-iron tubes of 2 inches bore, bent in the shape of a three-quarter circle (fig. 11) and connected by screwed-on flanges. With these there are no uneven places at the joints and no sharp angles as with the cast-iron worms. Even better than those tubes are wrought-iron worms each made in a single piece, as supplied by some Rhenish ironworks. These worms are always contained in circular iron tanks provided with a steam-pipe. Wrought-iron or lead worms cool better than cast-iron ones, owing to the less thickness of metal.

Fig. 11.



The total length of condensing-pipes is calculated in England at from 140 to 200 feet per still. In Germany the refrigerators are about 7 feet wide, and from 7 to 10 feet deep, with narrowly coiled worms, making the length of pipe from 200 to 300 feet, according to the size of the stills.

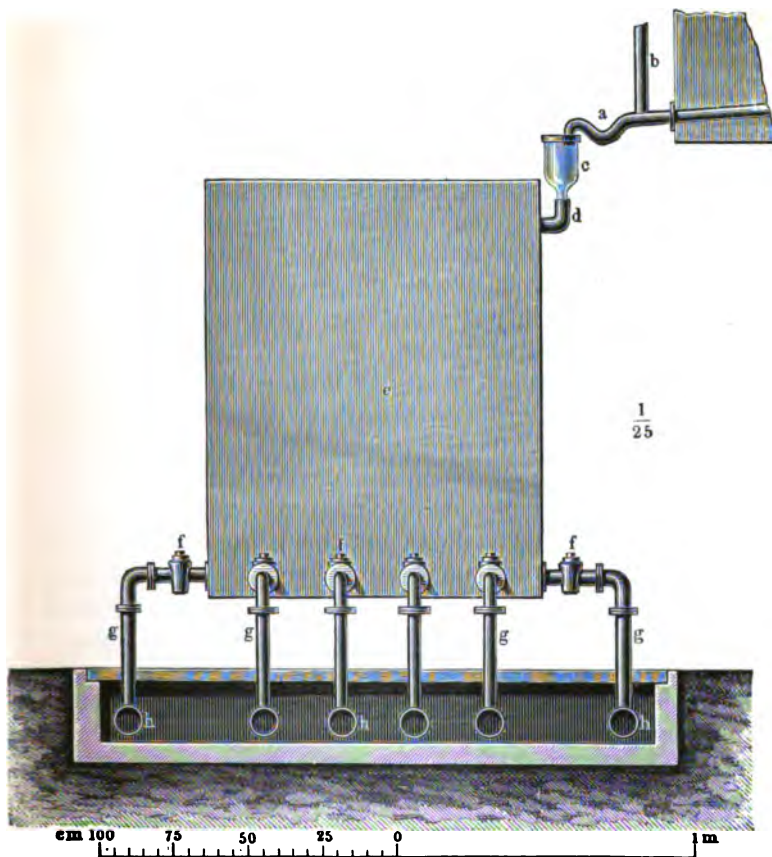
As *cement* for the joints the ordinary rust cement (made of iron borings, sulphur, and sal-ammoniac) can be employed. In lieu of this another cement may be used, which is as tight, but is more easily removed again. It is made by slaking lime to a powder, which is sifted and then kneaded with a little water to a stiff dough-like putty. This lime-putty is stemmed into the joints, hardens in 24 hours, and is perfectly tight against water and oils, either liquid or in the state of vapour; nor does heat affect it; only it must not be exposed to direct fire. For joining flanges, asbestos packing is no doubt the best possible material.

Instead of a condensing-worm, some employ a double cylinder with a current of water in the annular space between the cylinders. Such a contrivance is evidently safe against being stopped up.

Where the condensing-pipe comes out of the tank, it is slightly bent upwards (fig. 12 at *a*); and at this place an upright pipe *b* is fixed, through which the permanent gases escape, whilst the liquid products run into the receivers.

In order to separate the different products, there must be a corresponding number of *receivers*, and the products running out of *a* must be run at discretion into any of these. Evidently very many contrivances may serve for changing the receivers; but some points must be always observed. Thus the receivers for the first products must be tightly closed, to avoid both loss and danger of fire. Furthermore, the first receiver must be provided with

Fig. 12.



some contrivance for easily separating the oily and watery portions. The receivers for carbolic oil and those for heavy oils must be easily accessible, in order to remove the crystalline masses always separating in them. Above all, it is imperative to take every possible precaution against fire. If the receivers are placed near the tar-stills, they must be separated from them by a solid wall. Any tar which might by accident boil over and run out of the receivers, must under no circumstances be able to get near the still-fires or any other fireplaces. At some places the receivers are only just large enough to hold the product of one operation. This has the advantage that the manager can judge of the still-work by the depth of the liquor in the receivers; but then there

must be another and larger set of store-tanks for each fraction. Hence the receivers are frequently at once so constructed as to contain a large quantity of products, in which case they are placed at some distance from the stills and serve for a number of these at the same time.

Instead of dwelling upon the various ways in which receivers can be arranged, we prefer describing a special arrangement found at some of the largest works, and fulfilling the conditions of cleanliness, convenience, and safety. The distillates of each still run from the swan-neck pipe *a* (fig. 12) into the glass jar *c*, in which the process can be well observed. A jar with hydrometer can be placed in it; samples may be taken from it; the rate of distillation is easily observed; the appearance of the products is noted, &c. When the oils get too hot, it can be replaced by an iron funnel. The glass jar *c* is closed by a sheet-iron cover, cut out for the passage of the pipe *a*. It is fixed into an elbow pipe *d*, which conveys the liquids into the tight box *e*. To this are attached as many cocks *ff* as there are different fractions to collect. These are simple 2-inch gas-cocks, made of cast-iron; brass cannot be employed, on account of the ammoniacal liquor. The cocks *ff* (in our diagram there are six) are connected by flanges with the pipes *gg* which form vertical branches of the main pipes *hh*. The latter are laid in a bricked pit running along the whole set of stills, so that the products from all the stills pass into these pipes, which convey them ultimately into the store-tanks for each fraction. Care must be taken that the pipes *hh* have sufficient fall, and that the later distillates are not too much cooled in them, which would be sure to stop them up with naphthalene &c. Such cooling is partly prevented by covering over the pit with planks; but it is safer to put steam-pipes into the pipes conveying the later distillates. A special cock in the bottom of the collecting-box *e* permits samples to be taken and the contents to be run off at will. It is also possible to adapt this box to a continuous separation of the ammoniacal liquor; but this is an unnecessary complication, and it is more advisable to let this separation take place in the receivers.

The *receivers* or *store-tanks* for the various fractions may be of any shape,—square, cylindrical, etc. They are always made of wrought iron, and should be very well riveted and caulked; otherwise, especially if placed on the ground or even underground, great losses by leakage may occur before any thing is noticed,

which may even seriously contaminate neighbouring wells and watercourses. Even a previous testing with water will only reveal coarser leaks, as tar-oils penetrate much more easily through the joints than water. Hence the vessels must be closely observed for some time; if they are sunk in the ground there must be a free space left all round them for some days after they have been first taken into use, so that any leaks may be found out and stopped before the earth is filled in. The bottom of the vessels ought always to be formed of one piece. Of course the needful precautions against corrosion by rusting must be taken.

At some works, steamboiler-shaped cylinders (either horizontal or upright), which can be used at the same time for *forcing-up the oils by air pressure*, are preferred as receivers, or at least as store-tanks. Instead of pumping the liquids by means of ordinary pumps, which is very inconvenient with tar-oils, owing to the impossibility of employing fatty or india-rubber packings, they are now nearly always pumped by air pressure, compressed air being conveyed from an air-pump or blowing-engine to each of the receivers. This air presses on the surface of the oil and forces the liquids through ascending pipes, which reach down to the bottom of the vessel, and are provided with stop-cocks, to any suitable height or place. Hence the moving parts of the machinery are nowhere in contact with the oils.

Treatment of the Gases.

We have already mentioned the permanent gases formed in the distilling process. They are partly combustible; but it will hardly ever pay to utilize them in this respect, especially as that would entail considerable danger of fire. However much cooled, these gases at first carry away some of the most volatile of the tar-oils mechanically. Moreover they contain sulphuretted hydrogen, carbon bisulphide, perhaps carbon oxysulphide and other noxious gases, which may at times give rise to complaints of nuisance. Hence it will sometimes be necessary to subject the gases to a purifying process. An apparatus for this purpose, substantially as employed at a large London tar-works, is shown in figs. 13 and 14. The gas-pipes of all the cooling-worms are connected with a main pipe, which ultimately descends at *a* and enters the box *b c*. This is divided into two parts by a partition *d*, which does not reach quite to the bottom. The compartment *b* is empty, with

Fig. 13.

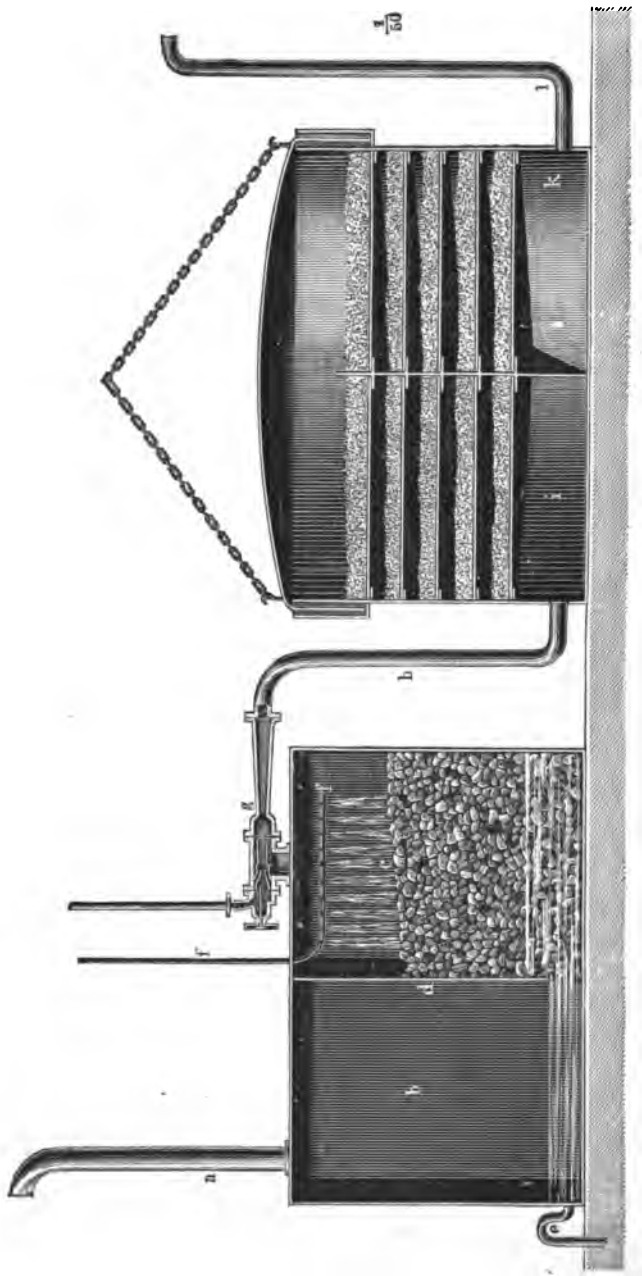
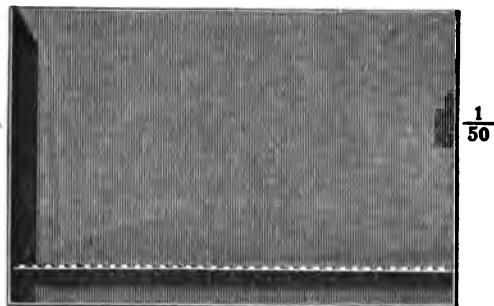


Fig. 14.



the exception of a little water at the bottom, which is kept level with the lower edge of the partition *d* by means of the overflow pipe *e*. The compartment *c* is filled with coke or some other material presenting a large surface, and constantly moistened with water by means of the perforated cross *f*. This compartment serves as a scrubber: the gas is washed by the water; and at the same time the oily parts are condensed, owing to the slackening of the speed of the gases, the friction upon the surface of the coke, and the rinsing action of the water. It seems preferable to assist the division of the gas into many jets by nicking out the lower edge of the partition *d*, as shown in fig. 14. In most cases the gas will be allowed to escape by means of a pipe put on the top of *c*, either into the open air or into a chimney; only provision must be made for preventing the water in *b* from rising quite up to the partition *d*, so that the gas can pass through. But where it is desirable to prove to the public that no precaution against nuisance is neglected, a further purifying-apparatus is added, say an oxide-of-iron purifier *i k*, from which the gas escapes at *l* into a chimney-flue. This purifier is exactly like those used at the gas-works, but on a much smaller scale. If the washing in *c* is to be made especially good, the gas is forced right through the water by means of an injector *g*, which takes it through *h* to *i*. The liquid hydrocarbons are all retained in the vessel *b c*; the sulphuretted hydrogen is absorbed in the purifier *i k*; and the last remnant of the smelling gases is made innocuous in the hot fire-flue into which it passes through *l*.

Working of the Tar-stills.

The stills are charged with fresh tar while they are still hot

from the last operation, but not so hot that they might suffer damage from the cold tar,—that is, a few hours after running off the pitch. The tar is either pumped in directly or run in from a higher tank previously filled. In both cases the bore of the feed-pipe is wide enough for the charging not to take too much time, say 6 inches; the air escapes by an air-cock or by the overflow cock *s*, fig. 4, p. 97. The latter also makes any other gauging of the contents of the still unnecessary. Where it is absent, the level of the tar must be ascertained by a float, or by a gauge-rod introduced into a hole, afterwards closed by a screw plug. The stills may be filled up to the point where the cylindrical part merges into the dome-shaped one. Watson Smith states the permissible level at 9 to 12 inches below the man-hole—with thin tars, 18 inches below the same.

All the openings are now closed and the firing commenced. The heating-up may even be begun when the still is only half filled, as the level of the tar is then above the flues; although the air-cock is then open, no loss is incurred, because the heating-up of the large bulk of tar takes much time, and the new tar running in causes a constant cooling. As soon as the charge is all in the still and the openings are closed, the fire is increased; and this is continued up to the point at which distillation is about to commence. This will take more or less time, according to the size of the still and the season; with small stills (5-ton charge) it takes about two hours, with large ones (20 to 25 tons charge) it takes five hours in summer, six hours in winter. One or two hours after the commencement of firing, the tar begins to rise and froth; and now the greater part of the ammoniacal liquor can be run off by the overflow-cock. After this the firing must take place somewhat more cautiously, to avoid sudden boiling over, which might otherwise take place with the violence of an explosion. From this time to the beginning of the distillation the fireman must always be in his place, and must watch the worm. As soon as the first drops appear at the end of the refrigerator, he must open the fire-door and slacken the fire; for now the danger of boiling over is greatest. With proper management of the still this ought *never* to occur; but if it does take place, it is little use opening the fire-door, letting down the damper, &c., because the mass of heat stored up in the tar, the iron, and brickwork is too great. Even completely drawing out the fire (which can only be done if the

still is quite isolated) does not act instantaneously. But it does good to pour cold water onto the still-top; and the same means must be resorted to whenever for any reason the distillation is to be stopped as quickly as possible.

The following are signs that distillation is about to begin:—Vapours issue from the end of the cooling-pipe, often in puffs, and gradually drops are condensed from them. The still-head gets warm, and the worm also where it is not yet covered by the cooling-water. Now in any case the fire must be slackened; for the distillation will commence directly. This is still more necessary as soon as a continuous jet of liquid comes out of the worm; it is then time to open the fire-door, or, what is better, to let down the damper. If at this stage there is any excess of heating, the ebullition takes place with violent bumping and frothing up, and in the worst case the mass suddenly swells up and boils over. The tendency to eruptive ebullition is imparted to the tar by the water contained in it, and is all the greater the more water is present. It has been mentioned more than once how the quantity of water, and with it the bumping and frothing, can be diminished.

During the first period of the distillation permanent gases, water (containing ammonium compounds), and the most volatile tar-oils are given off, which always carry along some of the less volatile constituents, partly in consequence of the vapour-tension of the latter, partly mechanically. During this period the cooling-tank must be well supplied with cold water, both for condensing the tar-oils and because the condensation of the steam and ammonia liberates much heat. A 1-inch water-pipe and 15 feet head of water will supply a cooling-tank for a 20-ton still.

Almost everywhere the *first fraction* is that portion of the oils which comes over along with water; so that the first receiver contains both ammoniacal liquor and tar-oils. The latter are called first runnings, first light oils, crude naphtha, &c. Water will form a greater or smaller proportion of the distillate, according to whether it had been previously removed or not; this proportion is ascertained by catching some of the distillate in a glass cylinder, in which naphtha and water separate at once, the former floating on the top of the water. At first much water and little oil comes, then less water and more oil; sometimes the time when the water ceases to come over can be fixed pretty sharply for changing the receiver. / But it is safer to wait till the distillation slackens. This is called

the "break," and is probably caused by the fact that the aqueous vapour carries along a quantity of oils of much higher boiling-point than that of water; so that, after all, the water is removed first. The temperature has to rise a good deal before the liquid begins to boil anew. At this stage sometimes for two hours hardly any thing comes over but a little water; and, from the peculiar noise made by the steam within the still, this period is sometimes called the "rattles." The rattling noise ceases when the temperature has risen high enough; and the distillate then comes over in a thick, quiet stream. It is now mostly collected in another receiver as "light oil," or "second light oils."

The ceasing of the appearance of water is not by itself a sufficient signal for changing the receiver; for sometimes a little water comes all along with the light oil, and even, at first, with the heavy oil, from the hydration water of phenol. Hence other signals must be the smell, the specific gravity, and the quantity of the distillate, or else the indications of the thermometer. The smell, which of course cannot be very well defined, generally shows the attendant quite clearly when he must change the receiver for light oil: the first runnings smell much more pungent than the light oil; and the transition is pretty sharp. The specific gravity increases slowly, and does not in this case give very distinct guidance.

If the fractions are to be made according to the indications of the thermometer fixed in the still (p. 102), it is usual to change at the following points:—

1. First runnings, up to 105° or 110° C.
2. Light oil, up to 210°.
3. Carbolic oil (for phenol and naphthalene), up to 240°.
4. Creosote oil, up to 270°.
5. Anthracene oil, above that.

These points are, of course, not always the same, partly because the thermometers do not reach down exactly to the same depth. Thus a large German works changes as follows:—

1. Light oils, up to 165° or 170°.
2. Middle oils (for carbolic acid and naphthalene), up to 230°.
3. Creosote oil, up to 270°.
4. Anthracene oil, above that.

Girard and DeLaire (loc. cit. p. 10) quote the following fractions:—

1. Huiles légères, from 30–140°, sp. gr. 0·780–0·850.
2. Huiles moyennes, „ 150–210°, „ 0·830–0·890.
3. Huiles lourdes, „ 220–350°, „ 0·920–0·930.

(The specific gravities are evidently wrong, and, no doubt, again prove an unaccountable confusion with paraffine oils.)

In the case of tars of known quality, the time and the quantity of the distillate are among the most important signals for changing the receivers. The former varies of course with the size and even with the shape of the still, its setting, &c. We shall make some statements on this point and on the quantity of the different fractions at the end of this chapter. The quantity of the distillate can only serve as a guide where each still has its own receivers, which is rarely the case at large works.

Attempts have been made to greatly increase the number of fractions at the first distillation of coal-tar, with the view of better isolating the products therefrom. All such attempts have failed hitherto, and probably will continue to do so in future. In no case are pure products obtained; and hardly any of the subsequent rectifications are saved; so that the whole is but a superfluous complication of the process. This is founded on *the nature of fractional distillation*, which has only recently been cleared up by a number of researches*.

The various components of a mixture do not distil simply in the order of their boiling-points, not even taking into account the vapour-tension of the substances not yet arrived at their boiling-point; but their vapour-density must also be taken into account. According to Dossios and Wanklyn, the quantity of each component distilling at a certain temperature is found by multiplying its vapour-tension at the boiling-point of the mixture into its vapour-density, or, what comes to the same thing, its molecular weight. Thus methylic alcohol (molecular weight = 32) boils at 66°, methylic iodide (molec. weight = 142) at 72°; but from a mixture of the two, more of the latter distils over. A mixture of 91 parts carbon bisulphide (boiling-point 47°) and 9 parts alcohol (boiling-point 78°) boils constantly at 43–44°, and during distillation retains its composition. Hence the liquid possessing the highest vapour-tension does not necessarily distil most rapidly; for what its com-

* Dossios, Jahresh. f. Chem. 1867, p. 92; Wanklyn, Philos. Mag. (4) xlv. p. 129; Glashan, *ibid.* p. 273; Naumann (*comp. below*); Thorpe, Journ. Chem. Soc. 1879, xxxv. p. 544; F. D. Brown, *ibid.* p. 547; 1881, xxxix. p. 304, &c.

panions lack in tension they may make up in vapour-density. If the tension is called t , the vapour-density d , we have for different liquids $x = ktd$, in which the formula k is a constant to be found by experiment in each single case. If the vapour-densities and tensions are inversely proportional to each other, and the values of k are equal, the products $k_n t_n d_n$ will all be the same; *i. e.* the mixture will remain unchanged throughout the distillation. For this reason homologous series (*i. e.* those whose members differ from each other by CH_2) are not easily separated by fractionating; for whilst the vapour-tension is lowered by each CH_2 , the vapour-density rises. This explains why so many substances distil more quickly in a current of steam; for aqueous vapour is one of the lightest bodies. By diminishing the pressure the difference between the vapour-tensions of different liquids is increased, whilst their vapour-densities remain the same*; hence they are more easily separated, as is proved by the success of exhaustion in gas-making and tar-distilling (see below).

A mixture of two liquids which are not mutually soluble, on distillation exhibits a boiling-point below that of the more volatile substance. A mixture of carbon bisulphide (boiling-point 47°) and water boils at 43° &c. This observation has been generalized by Naumann †, who found that the boiling-point of such a mixture is constantly below that of the most volatile component,—and also that the proportion of substance is always the same, *viz.* equal to the proportion of the vapour-tensions of the two components, measured at the temperature of boiling, multiplied by their molecular weights. This behaviour is of importance to us in tar-distilling also, where water boils along with oils not miscible with it. Thus, although at 98° the vapour-tension of naphthalene is only 20 millim., that of water 712 millim., yet at that temperature 49.4 grams of water pass over with 8.9 grams of naphthalene.

It is hardly necessary to mention that the different fractions are not divided by any sharp lines; and that at different works they are taken differently. In some places no distinction is made between first runnings and light oils, but all that has a specific gravity below 1.0 is taken as crude naphtha. The subsequent treatment must be adapted to this.

In any case *first runnings* and (aqueous) *ammoniacal liquor* come

* Winkelmann, Poggend. Annal. N. F. i. p. 430.

† Ber. deutsch. chem. Ges. 1877, p. 1421; 1879, pp. 2014, 2099.

together, the former floating on the latter. The latter is worked up like any other similar liquor, as will be described in the last chapter. The two liquids at once separate sharply: the water is either pumped away from below, or is continuously carried away by a pipe starting from the bottom of the receiver and turned upwards; or else the same object is obtained by a partition reaching nearly to the bottom of the receiver, or in any other way.

Light Oil.

The *second fraction* (if the distillate coming over before the carbolic oil is, as usual, divided into two fractions) begins after the "break," when the distillation proceeds quite smoothly, in a full stream and without any further danger of boiling over. The product is no longer a naphtha, but has a more oily nature; it is called either "light oil" or else "second light oil." We shall in future use the former name in this restricted sense. This fraction is usually continued up to the point where its specific gravity is equal to that of water. The men run a few drops into a cylinder partly filled with water; if the oil floats anywhere within the water in single, large, globular drops, its specific gravity is $=1.0$, and it is now time to change the receiver for carbolic oil. Where the fractions are made by the thermometer, this point will be at about 210° . This proves that the light oil must contain a good deal of carbolic acid (b.-p. 180°) and naphthalene (b.-p. 217°); but it must be remembered that in the upper part of the still and in the still-head some cooling takes place and the vapours partly condense again; hence the principal part, especially of naphthalene, only comes with the next fraction. But where carbolic acid and naphthalene are principal considerations, the fractionation is managed accordingly. This is the object of the style of working mentioned on p. 114, where the "middle oil," passing over between 165° or 170° and 230° will comprise nearly all the phenol and naphthalene, especially if the bulb of the thermometer is not placed in the tar, but in the liquid.

Another signal, sometimes used, for changing from light oil to the next fraction is obtained by letting a few drops of the distillate fall upon a cold piece of iron. If a crystallization of naphthalene sets in, it is time for changing. But this only holds good where no "carbolic oil" is separately received.

During the time the light oil is coming over (that is, after the break), the fire is increased without any danger of boiling over, although even now for the most part a little water appears, probably owing to the hydrate of phenol splitting up. Now the cooling-water begins to get warm; but little or no fresh water is run in; so that at the end of this stage the temperature of the water surrounding the worm is about 40°. If the work is arranged for "middle oil" in the above-mentioned sense, the water must be at least from 50° to 60°. Afterwards no fresh water at all must be run in; and sometimes even steam must be blown into the cooling-tank by means of a pipe entering at its *bottom* and pierced with numerous holes (*b*, fig. 8, p. 104): this is necessary because the danger of the worm being choked up is greatest in the bottom coils. Such a danger sets in even more near the end of the process, as we shall see afterwards; but it can be always provided against by allowing the water to get hot. Some English tar-distillers have not even steam-pipes in their refrigerators; but this is advisable in any case.

If the temperature in the refrigerator were kept too low, in the later period of the light-oil stage naphthalene would crystallize and choke up the worm, thus producing a dangerous pressure in the still. The explosions of tar-stills, rare as they are, are probably always caused by neglect in this respect, either during the naphthalene- or the anthracene-period. On the other hand, the water should not be allowed to get warm at the beginning of the light-oil stage, because then considerable quantities of the more volatile hydrocarbons are still coming over. This seems to be another reason for continuing the first fraction till benzene and all its homologues have passed over, and then condensing the "middle oil" with warm cooling-water.

Whether the worm is choked up, or not, is best seen at the end of the pipe coming out of the refrigerator, where it is curved up to allow the permanent gases to be taken away. This pipe should be warm; and the liquid should run out uninterruptedly: this is readily seen when it runs into a glass jar (*c*, fig. 12, p. 107). Where there is an intermediate vessel (*e*, fig. 12) with cocks for the different fractions, the distillate might possibly crystallize in this, or in the pipes *g g* that carry away the products. This is not so very dangerous, because the whole box *e* must be first filled with crystals before the worm can be choked up; notice will be given of it by

the box *e* or the cocks *f* getting cold. If the pipes *h* are sunk in the ground, if they are covered up, if they have sufficient fall and are not too long, they will not be easily stopped up; but it is decidedly advisable to be prepared for that contingency by making provision for blowing steam through them.

Where the work is carried on with evacuation by an air-pump or an injector, in the manner to be described hereafter, there is absolutely no danger of any choking up of the worm. But in any case the stills ought to be provided with a safety-valve or an equivalent contrivance (p. 102).

J. Vaughan * proposes preventing explosions that might occur in consequence of the worm choking up, by means of a wide pipe reaching nearly to the bottom and passing out at the top, connected with a large empty cylindrical boiler placed near the still and at a lower level. The connecting-pipe is enlarged at the highest point, and at this place is closed by a valve kept down by its own weight. The whole of the pipe is kept warm. If any excessive tension should occur within the still, the tar will rise in the pipe, lift the valve, and flow over into the empty cylinder. This is evidently exactly the same thing as that practised in Germany many years ago (p. 102).

Carbolic Oil.

The distillate at and above the specific gravity 1·0 was formerly not fractionated at all, but collected all together as heavy oil, dead oil, or creosote oil, and sold for pickling timber, without any further manipulation. Only exceptionally could the first and the last portion of the creosote oil be separately sold, the former for carbolic acid, the latter for lubricating-grease. When carbolic acid was aimed at, there was but rarely a special fraction made for it; the light oil was only driven a little further. No doubt phenol and its homologues, as we shall see in the 7th Chapter, occur also further on in the heavy oil, and constitute a great part of its value for preserving wood; but making pure phenol from proper heavy oil is rather difficult and expensive, and only takes place exceptionally. For this reason, since large quantities of phenol have been required for the manufacture of colours, for disinfecting, and for medicinal purposes, it has become usual to make a special

* Engineer, 1880, v. p. 298.

fraction containing as much carbolic acid as possible and with it a great deal of naphthalene. Although the boiling-points of these compounds are wide apart (180° and 217°), a large quantity of naphthalene is carried over below its boiling-point, and, on the other hand, phenol is kept back in the tar-oils above its boiling-point. Where no thermometer is placed in the tar-stills, this fraction is made to commence whenever the specific gravity of the distillate is 1.0; moreover its yellower colour and its smell serve as guides. A certain quantity of the oil now passing over is received as "carbolic oil;" and when this quantity has come over, the change for creosote oil is made. The amount of carbolic oil is usually 100 gallons from a charge of 2000 to 2500 gallons, *i. e.* 4 or 5 per cent of the tar.

In Germany it is usual (as it is more rational) to consult the thermometer. We have already mentioned that at some works the fraction passing over between 210° and 240° was taken as carbolic oil (probably the bulb of the thermometer dipped in the liquid itself), whilst at another (very large and well conducted) works the "middle oil" was received between 170° and 230° . The latter course seems most worthy of being recommended, as it leaves a suitable margin below the boiling-point of phenol and above that of naphthalene.

If the oils on cooling show a large crystallization of naphthalene, this is a sign that most of the phenol has already come before, or that it is now time to change for creosote oil; for naphthalene is much more soluble in phenols than in the heavy indifferent tar-oils, and hence mostly remains dissolved in the distillate as long as there are considerable quantities of phenols present, but crystallizes in large masses on cooling when the phenols are becoming scanty; but this rule is not without exceptions.

Each factory must, of course, find out for itself which are the proper limits of this fraction: they will depend upon the size and contents of the stills, the position of the thermometer, the quantity of the tar, &c. The criterion is that the crude carbolic acid, obtained by the subsequent treatment of the carbolic oil, is of the proper quality, as will be explained in the 8th Chapter. As far as naphthalene is concerned, enough of it is sure to come over; and sometimes it crystallizes out in large quantities. Only exceptionally does tar contain so little naphthalene that it is not partly separated in the solid state. Hence the previously-mentioned pre-

cautions for preventing the choking-up of the pipes should be always observed in this case.

Creosote Oil.

The fraction which comes over after the carbolic oil generally contains at first sufficient naphthalene for some of it to crystallize on cooling in a shallow dish. But after some time this ceases; the naphthalene, still present, but in smaller quantity, remains dissolved in the liquid hydrocarbons even after cooling; and as phenol and its homologues, which impart to the products the property of promoting friction, have ceased even before, the portions now received possess a milder, more oily or greasy nature, which makes them suitable for cart-grease. Hence this product is sometimes called "soft oil." It generally begins to appear when about half of the heavy oil (calculating for a distillation up to hard pitch) has been received. Before an industrial use had been found for the anthracene oil, sometimes the second half of the heavy oil, *i. e.* the "soft oil," along with the "red oil" or anthracene oil, was run into a special receiver as "grease oil," sometimes separating the liquid soft oil from the butter-like grease. This was done chiefly in the first years after 1860, when, owing to the American civil war, the price of rosin had risen enormously, and the cart-grease-makers were glad to get any substitutes for rosin-oil. The liquid soft oil was sometimes called "yellow creosote," from its yellowish-green colour, which soon, however, changes into dark brown. Its value as a lubricant was inferior to that of the last portion, the "solid creosote" or a green grease answering to the present anthracene oil. In any case these products are very much inferior as lubricants to rosin-oil or lubricating oils from petroleum and paraffine-oil refineries. The separation of yellow from solid creosote is probably very rarely made now for the purpose of obtaining a lubricant, but to obtain, in the "*anthracene oil*," that constituent of coal-tar (*viz.* anthracene) which, since Graebe and Liebermann's discovery of artificial alizarine (1868), has become far the most valuable product of this industry. All the remaining heavy oils are put to the uses to be described in the 7th Chapter.

Anthracene Oil.

The beginning of the anthracene-oil period is either judged by outward marks or by the thermometer, sometimes by the quantity of the distillate. Usually it is calculated that about one sixth of the heavy oil (reckoning from sp. gr. 1.0 up to hard pitch) comes as anthracene oil. The latter may be reckoned to begin when the oil ceases to remain liquid after complete cooling—that is, when a fresh separation of solids sets in. Where the thermometer is employed, 270° is nearly everywhere assumed as the commencing-point. Probably this general consent results from the fact that from this stage the thermometer-bulb is universally in the vapour. Sometimes first and second “green oil” or “red oil” are received separately.

End of the Distillation.

Formerly this was decided according to whether hard or soft pitch was to be left in the still. Sometimes, but rarely, the work was stopped as soon as all the light oil had passed over; the residue then remaining in the still was called “asphalt,” and was employed in the paving of streets, for protecting underground iron tanks from corrosion, and similar purposes (see next chapter). But the work was nearly always continued further, either up to soft pitch or hard pitch (*brai gras* and *brai sec*). Soft pitch is obtained when only half the dead oil is distilled off—that is, just as the “soft oil” is coming; moderately hard pitch, when the soft oil and the first portions of anthracene oil are taken away; hard pitch, when the distillation is carried to its conclusion, as will be described presently. The special characters of these different descriptions of pitch will be given in the next chapter.

Since anthracene has become the most valuable product of tar-distillation, wherever the tar is not very poor in anthracene (comp. p. 13) the distillation is mostly continued till hard pitch is produced. In England and France it is usually run out in this state; in Germany they manage differently, as we shall see.

In the last period of the distillation the water-supply to the worm-tub must be shut off altogether, and the water in the tub must be allowed to boil; if necessary, ebullition must be produced by blowing in steam.

The distillate which now separates is a mixture of anthracene,

phenanthrene, carbazol, &c., later on also of chrysene, pyrene, &c., and ultimately contains so much of these that on cooling it solidifies into a butter-like mass which would choke up all the pipes. This must of course be avoided by keeping the worm-tub and the conveying-pipes warm, or even (more safely) by employing steam; but the best way of all is by producing a vacuum (see below). The oil running off should be about 60° C. If the distillation is continued till hard pitch is formed (*i. e.* pitch which will be hard when cold), it becomes at last very sluggish; its cessation is determined by the manner in which the distillate solidifies, and by its quantity—also by the time elapsed, and by the peculiar smell, now again changing. Steam being usually injected now, the thermometer is of no further use; and in any case a mercurial thermometer could not be employed at this stage, the temperature in the interior of the still being about 400°. In the case of tars containing too little anthracene &c. to solidify, the other signs must suffice for judging when to stop. Frequently, also, the hydrometer is consulted. If the distillate shows a specific gravity = 1.080–1.090, the residue will be moderately hard pitch; at 1.120 it will be hard pitch; but this does not hold good of all descriptions of coal-tar, and should be tested by experiment.

If the distillation is continued too long, much damage is done in more ways than one. In the first place, the anthracene is too much contaminated with chrysene and pyrene; again, the pitch is half coked: in the worst case it ceases to run out of the still; and even if it does run, it does not solidify in a glass-like, but in a porous, honey-combed form and is quite unsaleable. Lastly, the still itself is much damaged by this treatment.

E. Kopp* proposed driving off only a portion of the creosote oil and *distilling the soft pitch to hard pitch in a special still*. He asserted that he had found in such soft pitch from the Turin gas-works 4 to 6 per cent. anthracene; but this seems very improbable, and it should be remembered that at that time no exact methods for estimating anthracene were in existence. The pitch-still was to have a greater width than depth; the gas-pipe was to be of large bore, to join the still only 6 or 8 inches above the level of the boiling pitch, and then to bend down at once, in order to carry away more readily the heavy vapours. Towards the end the distillation was to be promoted by a current of superheated

* Bolley-Kopp's 'Gespinnstfasern,' p. 381.

steam, or of heated air which had been passed through a red-hot pipe filled with charcoal, and thus converted into a mixture of carbon monoxide and nitrogen. During the distillation as much melted pitch as corresponded to the oil distilled was to be run into the still by means of a pipe reaching through the still-cover half-way down into the pitch; this would amount to half as much as the original charge of pitch in the still. The steam or heated gas was to issue either immediately above the surface of the boiling pitch or within the same. Lastly, when the contents of the still had become too thick they were to be expelled by the steam or air, the cooling-worm having first been shut off. We do not know whether Kopp's proposal has ever been carried out in practice. That part of it which refers to promoting the distillation by a current of steam or gas, has been proposed and carried out elsewhere (see below). There remains the proposal to effect the distillation to hard pitch not in the same still from beginning to end, but transferring the last stage to a separate vessel. This would not pay unless more anthracene were got out, which has not proved to be the case.

We must distinguish between this distillation of soft pitch up to the stage of hard pitch, and that of hard pitch itself to coke, which will be described in the next chapter.

Employment of Steam, or of a Vacuum, &c. in the last Stage of the Process.

Apart from what would happen if hard pitch were run off too soon, the still-bottom naturally suffers considerably during the last stage of the process, when the heat has risen to a high point, especially where it is not protected by a curtain arch. At the same time the vapours now formed, which are very heavy, cannot so easily get out of the still into the worm, the level of the mass being now very low, and the upper part of the still not being heated; a portion of these vapours must condense again within the still itself; and the distillation is but sluggish. The longer it lasts, the more opportunity there is for the hydrocarbons to split up into carbon and permanent gases (p. 11). Hence it seems rational to promote the carrying-away of the vapours at this stage, either by superheated steam &c., or by a vacuum, or both.

Steam seems to have been employed for a long time past to

promote the distillation, not merely at the commencement, as described, p. 87 *et seq.*, but again in the last stage*, when it must, of course, be first superheated. It then fulfils more purposes than one. It assists in carrying away the vapours as before mentioned; this shortens the time required for the distillation, and increases the yield; besides, it prevents the pipes from being choked up. Thirdly (and principally), the formation of hard crusts upon the still-bottom is lessened by the temperature just at that place being kept comparatively low, so that coking and burning-on of the pitch cannot easily take place. Indeed Trewby and Fenner assert that with their system, shown in figs. 4 & 5 (pp. 97, 98, 102), no coke at all is formed on the still-bottoms, and thus cleaning-out the still becomes unnecessary. Elsewhere experience has not been quite so favourable, but perhaps because the steam was introduced by means of a simple cross of tubes, &c., whilst by Trewby and Fenner's plan steam ranges over every part of the still-bottom, issuing from numerous and suitably-formed outlets. For this reason we have adopted their system (introduced at the great Beckettou works) in our diagrams, without undertaking any responsibility if it should be found too complicated, and the outlets too liable to be choked up.

A further question is, in what way is the steam to be superheated? At a German works the superheater is a coil of $\frac{3}{4}$ -inch wrought-iron tubing, with a bottom surface of 3 feet 3 inches square, placed in an oven-like space above the fire-arch. The boiler-steam is first freed from liquid water in a suitable catch-pot, and then enters the superheater, where it attains a temperature of 275° C. The steam-pipe, where it issues again, is covered with a thick non-conducting coating, and runs over the top of the still (which has the shape of a steam-boiler), into which it sends four branches. Each of these is provided with its own cock, and also with a special air-cock, through which the steam is blown off for a moment in order to remove any condensed water, before the cock leading into the still is opened. This arrangement has been in operation ever since 1873, and gives perfect satisfaction. The steam is first blown in when the change is made for anthracene oil—that is, when the thermometer has got up to 270°. From

* *E.g.* Cormack's patent, No. 1368, June 2, 1864. According to Watson Smith, Mr. John Barrow, in Manchester, employed steam as a secret process about the same date.

this time to the end of the process no more firing takes place; the heat stored up in the arch that runs all along the still-bottom, together with the superheated steam, suffice to finish the distillation. After the anthracene oil has been got out, creosote oil is pumped into the still, to make soft pitch or "prepared tar" (compare Chapter V.), which lowers the temperature so far that the still can be emptied at once and recharged.

A similar system of completely dried and then superheated steam we found at another German works, employed with stills of the usual cylindrical form with concave bottom, and giving complete satisfaction.

Trewby and Fenner do not superheat the steam at all, as they find that in their system, where it is conducted through the tar in so many fine jets, it is by this alone superheated to the temperature of the tar; and they claim this as one of the advantages of their apparatus. But the author observed also at a German works, where the steam was simply introduced by a cross of tubes, that no special superheating took place, the superheater formerly employed having been dispensed with. But the steam was previously dried, and caution was always used in first starting it, as any water carried into the still would cause an explosion when suddenly brought into contact with tar standing at a temperature of 300° and above. This has actually taken place at more works than one. Just for that reason we would advise in any case such a slight previous superheating as will *completely* dry the steam, which can be done without any expense whatever.

Wurtz* mentions that at some English works the stills are furnished with *mechanical agitators* in order to avoid superheating the bottom at the end of the process. We do not know of any such arrangement existing in England. It has been patented by Audouin† along with agitation by means of a stream of illuminating-gas, carbon dioxide, air, or smoke-gases. It is asserted that in this way 10 to 15 per cent. more anthracene is got than usual.

The employment of dry steam at the last stage of the process has the further advantage that in running off the pitch no air need be admitted into the still, which might possibly lead to explosions or fire.

Cabot‡ seeks to promote the distillation of anthracene by blowing petroleum into the mass.

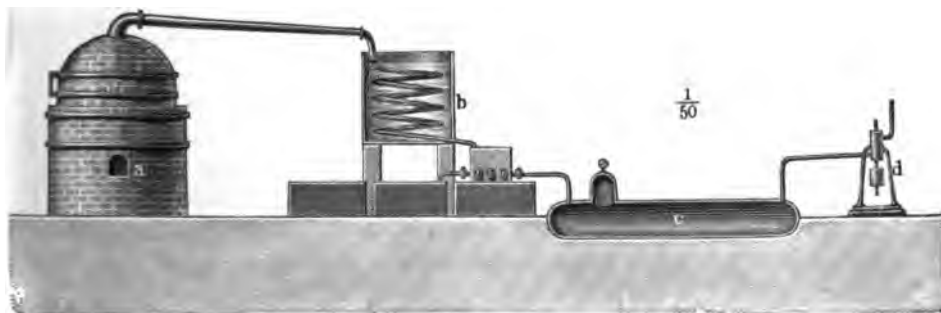
* *Matières colorantes*, p. 25.

† 13th May, 1872.

‡ Amer. pat. No. 184,142.

Excellent success is claimed for the *employment of a vacuum*, which the author saw in operation at a German works in the following manner. The distillation is commenced at the ordinary pressure, and continued till it is time to change for anthracene oil. Now a steam-pump is started, which aspirates both gases and oils away from the condensing-worm into a large boiler sunk in the ground, where the anthracene oil remains whilst the gas is forced out by the pump. From the same pipe steam is injected into the still, as above described, but merely to keep its bottom clear ; for no choking-up ever happens, even without the steam : the pump sucks away the butter-like mass quite easily into the boiler. The vacuum-gauge in this showed 15 millimetres mercurial pressure. On their way along this boiler the products were cooled, so that the gas coming out of the far end entered the pump nearly cold. When the distillation was finished, the same boiler served as a pressure-apparatus for forcing the oils into the anthracene-crystallizers. The whole arrangement answered so well, that a second apparatus of the same kind had been mounted for creosote oil ; but this had not yet started at the time of the author's visit. The greatest advantage of this plan is the regularity of working, and the complete absence of any danger of choking up the pipes. An injector had been tried in lieu of the steam-pump, but had not answered so well. The sketch (fig. 15)

Fig. 15.



may serve for elucidating the process. In this, *a* is the tar-still, *b* the condensing-worm, *c* the anthracene-oil-boiler with its dome, vacuum-gauge, steam-pipe, &c., *d* the air-pump.

Running-off the Pitch.

When working in the old manner (*i. e.* without steam &c.), it is necessary to fire up to the end, and that sharply. As soon as it is considered that the operation is at an end, the fire-door is opened, the coals are drawn out, and at once the distillation ceases. But the pitch cannot be run off at once, partly because there is danger of its taking fire, and partly because the large amount of heat stored up in the still and the brickwork, might damage the still. Hence some time must elapse before the pitch can be run off with the precautions prescribed above—two, six, or even twelve hours, according to the size of the still. After the pitch has been let out, again some hours must pass before coal-tar is pumped into the hot still, lest the sudden contraction on cooling should start the rivets &c. At first sight it would seem most suitable to wait rather longer before letting out the pitch, and thus further to diminish the danger of its taking fire; but it is much more important that the pitch should be perfectly liquid when run off, so as to leave the still completely empty. The outlet-cock must be arranged with the same view. Whatever pitch remains in the still is changed by the heat retained by the brickwork into coke, which covers the still-bottom as a non-conducting layer, does not dissolve in the fresh tar, and would soon cause the bottom to be burnt away, if it were not from time to time knocked off and cleaned out like boiler-scales. With ordinary English stills, this must be done after three or four distillations; but proper placing of the cock, protecting the bottom by a curtain-arch, and twelve hours waiting will prolong the time to about a month.

At the German works this operation is much simpler and easier, as they distil in the first instance to hard pitch, but then pump creosote oil back into the still, say 10 to 20 parts for 100 parts of pitch, the mixture of which with the hard pitch produces softer pitch of various qualities, or "prepared tar" (see next chapter). This process is made necessary by the impossibility of selling hard pitch there. In this case no choking-up of the outlet-cock, or taking fire of the pitch in the air on running off, need be feared; and crusts of coke at the still-bottom would probably not appear to any great extent, even if steam were not applied, which, however, is done almost everywhere.

An outlet-cock can be dispensed with altogether, if the pitch,

after some cooling, is forced out by means of perfectly dry steam through an upright pipe that comes out of the still-top and conveys the pitch to some safe place. The outlet-pipe should start from the bottom of the still (which in this case may even be convex), and rise perpendicularly to the highest point, and thence descend in a gentle curve; it must be heated up by steam before the forcing begins. There is in this case no danger of any fire in the pitch-house; and the process has answered very well indeed at German works.

Running-off the *soft* pitch (which is not so very hot, does not take fire in the air, and does not choke up the cock) is easy enough. But things are different when *hard* pitch is to be run off, as is usually the case in England and France. Here not merely must the pitch be allowed to cool down to some extent within the still, but it must first be run into a place protected from the air, in which it must remain till it gives off no more vapour and is no longer liable to take fire in contact with the air. Then it is let off into the open pitch-holes to solidify. In this case the outlet-cock of the tar-still should be provided with a cleaning-flange, and with some contrivance for heating it in order to melt the adhering pitch. This is best done at the end of each operation, before the still is charged again; it is then attended with much less danger than is incurred by deferring the heating till it is time to run off. For this purpose the plan shown in our diagram (fig. 16, p. 132) can be recommended. The cock is placed in a recess of the still-wall; and at each side of it, separated from it by thin walls, the flues descend. If this should not keep the cock warm enough, a small fire of wood shavings can be made round the cock in the recess; or this is filled with sand which is heated by a small fire. Sometimes a steam-coil is wound round the cock; but steam-heat is frequently not sufficient for melting hard pitch. In any case the cock must be situated at the opposite side to the fire-door, lest the vapours given off from the running pitch be set on fire.

The outlet-cock is connected by a short descending pipe with an iron or brick spout covered over with an iron plate, for conveying the pitch into a chamber where it is to undergo its first cooling (the pitch-house). A spout is preferable to a pipe, unless the pitch-house is immediately beside the still, because the pitch readily solidifies in this part of its course, which does less harm when it takes place in a spout than in a pipe. The cover of the

spout is covered over with earth to keep off the air and prevent cooling; but, for all that, there is always a coat of solidified pitch in it, which must be hacked out afterwards. If the air is not kept off here, the pitch may easily take fire; and the flame would travel to the pitch-house, in which case an explosion would be almost certain to follow. The spout must have sufficient fall and no sharp curves.

In the *pitch-house* the pitch must be left long enough (say five or six hours) to cease giving off vapours and to run no risk of taking fire when brought into the open air. This cannot be done without the pitch getting rather tough; hence a good deal of it remains behind in the pitch-house, and must be hacked out from time to time. The pitch-house is either a brick chamber with brick floor and arched top, or else any sort of iron vessel. A brick pitch-house for two 20-ton stills is about 20 feet long, 7 feet wide, and 8 feet high to the crown of the arch. Each gable end is provided with a 3-feet-square man-hole, closed by iron doors luted with clay. At one gable end the pitch-spout enters; and at the opposite one there is a tap-hole just above the bottom, plugged with clay or with an iron bar, from which open spouts lead to the different pitch-holes.

Iron pitch-chambers are either cylindrical or square; they are more expensive, and suffer more by the hacking out, but cool much quicker than brick chambers. The latter is no sensible advantage, since even in a brick chamber the pitch is cooled long before the chamber is needed for the next charge.

Sometimes no pitch-houses are provided; the pitch is then left to cool in the still itself till it can be run straight into the open pitch-holes. This plan is decidedly not advisable for *hard* pitch: the stills must be allowed to rest much longer; and they must be cleaned out by manual labour after each operation.

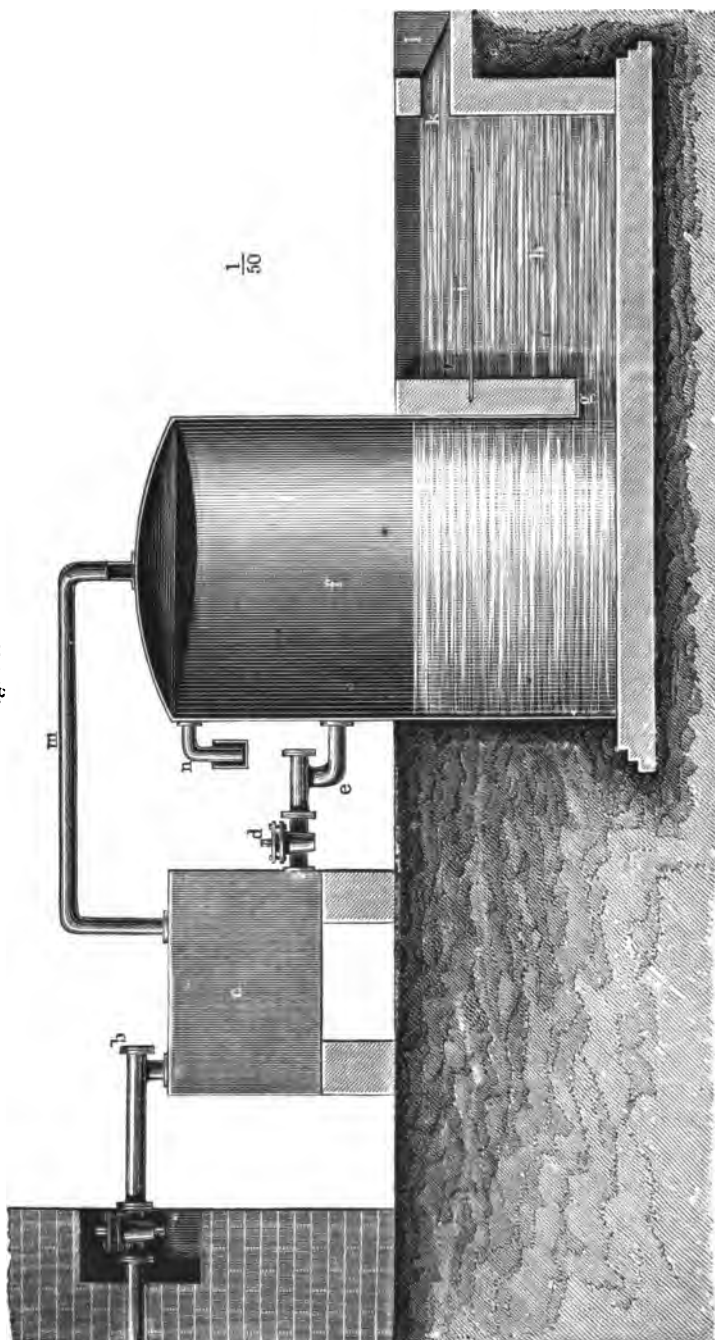
Lastly, the *pitch-holes* are situate in front of the pitch-house. They must have a perfectly level brick floor and 18-inch side walls; but otherwise their shape is quite indifferent and may be adapted to local circumstances. They ought to be of sufficient area to make it unnecessary for the pitch ever to fill them to a greater depth than 12 inches. There must be at least two of them, to serve in turn, so that at all times the pitch may completely cool down and solidify in one of them. In the heat of summer this is sometimes promoted by squirting water over. It is expedient to

whitewash the floor every time before using it again, to make it perfectly smooth and to facilitate detaching the pitch. Hard pitch becomes so brittle that it is easily hacked up with a pick in large lumps. The dust unavoidably formed is most irritating to the mucous membranes of the eyes; the men ought therefore to protect their eyes by "goggles" or by crape; and this kind of work is always done by preference at night. In summer it is of course more disagreeable than in winter.

Watson Smith points out that the pitch-holes ought to be laid out so that no pools of rain-water can remain in them; otherwise the pitch will be honeycombed and much less saleable.

Instead of the simple pitch-house just described, a more complete arrangement has been made at the Paris gas-works—an arrangement proposed by Regnault, and which is also found at a large English tar-works. It is represented in fig. 16. The pitch leaves the still by the cock *a* and a pipe *b* (provided with a cleaning-neck) and runs into the iron box *c*, in which it remains a few hours, till it has cooled down to 200° C. From this it goes through the cock *d* and the pipe *e*, into a wrought-iron chamber, *f*, half sunk in the ground, 7 feet wide, 30 feet long, and 10 feet deep, which receives the pitch of a number of stills. Along its whole length runs a brick pit *h*, 5 feet deep, communicating with *f* by holes *g* near the bottom. An iron plate, *i*, prevents the pitch as it comes from *f*, at a temperature of about 120° C., from rising at once to the surface; it can only pass along the edge of *i*. The pitch in *f* and *h* remains liquid from one operation to the next, being protected from quick cooling by the ground. But on the surface of the pitch above *i* a hard, elastic crust forms; this is promoted, if necessary, by running water over it. Now, if fresh, hot pitch runs out of *a*, it flows in *f* onto the surface of the partly cooled, but still liquid pitch from the last operation, forces this through *g* into *h*, the still colder contents of which rise past *i* and flow away underneath the crust at *k* into the open pits *l*, where they are left 8 or 10 days for entire solidification. The very hot pitch in *f* has in the interval time to cool down; the vapours rising from it and in *c*, which communicate by the pipe *m*, are condensed by the surface of iron in contact with the air, and are reabsorbed by the liquid pitch. The pipe *n*, which dips into a vessel filled with tar, allows the air to escape as the tar runs in, and also serves as a kind of safety-valve. But, besides, *f* is provided with a loose manhole-lid, merely

Fig. 16.



luted by Scott's cement &c., which likewise performs the office of a safety-valve. This apparatus completely does away with the nuisance arising from the heavy, yellow, extremely irritating vapour given off by the hot pitch, and with all danger of fire. The author, whilst seeing that pitch was being run off, by the flowing away of tough pitch from the hole *k*, could not perceive the slightest smell, although standing close by.

Continuous Distillation of Tar.

Several attempts have been made to render the distillation of tar a continuous operation, involving a constant inflow of fresh tar and outflow of pitch. Mallet * makes the tar circulate on a sufficiently long lead bath, where it successively gives off light and heavy oils, and at the end run off as pitch. The fractionating is effected by making the tar pass round divisions which do not impede its circulation, but separate the vapours into two or three classes. According to Knab, there is nothing gained by this plan.

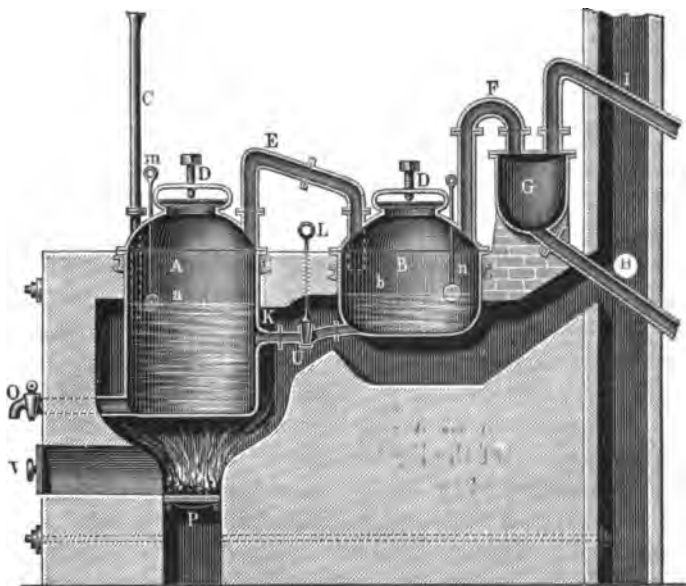
A proposal made by Vohl † is likewise intended to carry out a fractional distillation at a constant level, especially in order to meet the drawback of the light oils being kept back by the heavy ones. This is effected by the apparatus delineated in fig. 17. A and B are cast-iron stills; C, a feed-pipe dipping 3 or 4 inches into the liquid; DD, manhole-lids; E, pipe for conveying the vapours given off in A to B; F, pipe for the vapours going from B to the separator G; H, pipe for the heavy oils, connected with a refrigerator; I, pipe for the light oils, also connected with a worm; K, connecting-pipe between the two boilers, with the stop-cock U, to be opened and shut by the handle L, in order to let the liquid flow from B into A. *m* and *n* are floats; *m* is so arranged that, on the liquid in A rising above the level *a*, the float shuts the supply-cock of C; *n* is connected with a loose valve which opens whenever the level rises too high. O, outlet-cock for the heavy-oil residue in A; P, fireplace; V, stoking-hole. To start the apparatus, A is filled through C up to the level *a*, its contents heated to boiling, and then a continuous supply run in through C. Until the ebullition in A is very strong, the flame is kept off B by a damper, and is directed straight to the chimney.

* Girard & Delaire, 'Dérivés,' p. 11.

† Dingl. Journ. clxxvii. p. 133.

Meanwhile B and G are getting heated, and from H a constant stream of oil distils off. Now by opening the damper the fire from P is directed underneath B; and from this time light oils distil from I, heavy oils from H; the heaviest oils remain behind in B.

Fig. 17.



If *m* shuts off the supply-cock, the fire must be increased. Also if the valve *n* in B is lifted, this is a sign of too little firing, too much being condensed in B; or else the damper keeping off the fire from B has been raised too late. When A has been worked off, which is soon known by experience, the fire is damped by wet ashes and the residue from A let off through a refrigerator (consisting of a set of cast-iron pipes immersed in water) into a tightly covered iron vessel. Then the contents of B are run through U and K into A, the level is made up to *a* by supplying tar through C, the damper for B is let down, and the operation is recommenced. Such an apparatus (erected by Thiriart and Co. of Cologne) is said to yield $1\frac{1}{2}$ ton of light oils in 12 hours. It was originally intended for paraffin oils; but Vohl believes that it is also eminently suitable for coal-tar, and would yield twice the usual quantity of benzene and its homologues.

Results of Work.

In the case of tars of well-known quality the *duration of the distillation* and *the quantity of the distillates* furnish valuable indications for changing the receivers. The former must evidently vary much, according to the size and even the shape of the stills. The author has recently received the following statements respecting it.

In Paris the distillation of $6\frac{1}{2}$ tons lasts 31 or 32 hours, cooling included. The first runnings and light oil run 14 hours. The necessary fuel amounts to 50 cubic feet of "agglomerated coke" (patent fuel made from coke breeze).

At a London works a still of 2000 gallons (say 10 tons) capacity is worked off every 24 hours. 14 hours are reckoned for the distillation, 10 hours for cooling down, running the pitch, cooling again, and recharging.

Very small stills, of 1200 gallons (=6 tons) capacity, are all finished in 11 or 12 hours. The fire is slackened an hour after commencing; an hour later the distillation begins, and the heavy oils six hours after that.

At one German works the horizontal 18-ton stills take 52 hours for working off, and 12 hours for cooling. At another the stills (very large, holding 40 to 50 tons) take only from 36 to 42 hours for working off, and 6 hours for cooling. At a third works 25-ton stills take 36 hours.

At an English works known to the author the first runnings from a 22-ton still take 10 hours, the light oil (up to sp. gr. 1.0) 6 hours, creosote oil (including anthracene oil) 12 or 14 hours, cooling down till the pitch is run off 12 hours. Immediately after, the stills are recharged.

According to Watson Smith, in Lancashire 20-ton stills (steam being employed at the close) were worked off 4 times per week when anthracene oil was not worked for,—in the other case, three times per week, or 7 times per fortnight. 10-ton stills are worked off 6 times per week.

In the following we give the *yields* of the different fractions from coal-tar, from various sources. But these data are not directly comparable with one another, as we have seen that the fractionating is not done in the same way in all.

To simplify matters, we shall at the same time quote the quantity of the final products, wherever they are stated.

*Average of our own Results with 1 ton of tar from the
Midland Counties.*

Ammoniacal liquor... 3 gallons.
First runnings..... 5.5 to 8, average 6.33 gallons.
Light oil 13.5 to 15 gallons.
Creosote oil..... 68 gallons.
Pitch (hard)..... 11 cwt.

Final Products from the same.

	Average.	Minimum.
50-per-cent. benzol.....	3.30	3.06 gallons.
Best naphtha	2.40	2.48 "
Burning naphtha	1.50	1.62 "
Creosote oil directly distilled .	68	... "
" " total	80	80 "
Pitch (hard)	11 cwt.	11 cwt.

According to Stohmann-Kerl's 'Chemie,' 3rd ed. vi. p. 1169:—

	South-German tar.	North-German tar.	
	per cent.	per cent.	
		a.	b.
Light oil	10.5	8.4	8.9
Middle oil	9.4	10.6
Creosote oil	27	23.9	24.6
Pitch	57	50.9	50.9
Ammoniacal liquor and loss ..	5.5	7.4	5.9

According to Thenius (Deutsche Industrie-Zeit. 1865, p. 292):—

	Ordinary gas-tar.	Tar made as principal product.	Tar obtained on purpose by distil- ling coal with superheated steam.
	per cent.	per cent.	per cent.
Ammoniacal liquor	4.0	4.00	6.22
Light oil (sp. gr. 0.900) ...	4.0	30.32	25.34
Creosote oil (sp. gr. 1.020).	32.0	38.13	32.53
Paraffin oil	13.68
Pitch	56.0	18.75	16.03
Gases and loss	4.0	8.50	6.20

According to Wurtz ('Matières colorantes') 1000 kilog. tar, value 90 francs, yield :—

	a.	b.	c.
	kg.	kg.	kg. fr.
Ammoniacal liquor	14	14
First runnings }	18-20	{ 20-40	20 = 10·00
Light oil }		{ 70-80	70 = 35·00
Creosote oil	240-280	320-350	320 = 48·00
Anthracene oil, 10-per-cent. .	9·5-10	100-110	100 = 60·00
Pitch	660-650	350	350 = 17·50
			170·50

[The enormous difference between the columns *a* and *b* is inexplicable. It seems hardly credible that tar could be worked down to 35 per cent. of even very hard pitch. Neither can 100 kilog. of 10-per-cent. anthracene oil, *i. e.* 1 per cent. of real anthracene, be obtained.]

Tar from the Berlin Gas-works (Chemische Industrie, 1879, p. 282).

	per cent.	per cent.
Benzol (including toluene &c.)	0·80	
Other white oils (higher homologues) .	0·60	
Crystallized carbolic acid	0·20	
Cresol for disinfecting-purposes	0·30	
Naphthalene	3·70	
	—	5·60
Creosote oil		24·00
Anthracene (pure)		0·20
Pitch		55·00
Water and loss		15·20
		100·00

The following statements are from 'Chemistry, by Writers of Eminence,' Mackenzie, i. pp. 500 and 506.

The average produce from 1200 gallons of tar (about 6 tons) is :—

			per cent. by weight.
Ammoniacal liquor ...	about 50 gal.	= about	4
First light oils	„ 20 „ „		1.5
Second light oils	„ 20 „ „		1.5
Creosote oils	„ 250 „ „		22
Anthracene oils	„ 50 „ „		4
Pitch	„ 4 tons „		67

According to Letheby, 1 ton of gas-coal, as distilled in London, gives about 9 to 10 gallons of tar; 1 ton of coal as distilled in the provinces gives about 15 gallons of tar; 1000 gallons of London tar yield:—

Ammoniacal liquor.....	20-28 gal., average	24 gal.
Crude naphtha (first light oils)	12-20 „	16 „
Second light oils	4.8-14 „	12 „
Creosote oils	275-296 „	288 „
Pitch	3.2-4 tons, „	3.5 tons.

After purification these light oils yield:—

	gallons.	
40-per-cent. benzol ...	3.44	} = 6.84 at 90 per cent.
90 „ „ ...	5.31	
Solvent naphtha	4.18	
Last runnings	1.2	
Total dead oils	301.87	

Watson Smith obtained in 1869, from Lancashire tar [mostly made from cannel coal], as follows. 1000 gallons of tar of sp. gr. 1.16 = 5.3 tons, yield:—

		per cent. by weight.
Ammoniacal liquor (4-per-cent.).	25 gal., =	2.2
First light oils	28 „ =	2.2
Second light oils	131 „ =	10.6
Creosote oils	87 „ =	7.6
Anthracene oils	191 „ =	16.9
Pitch	3½ tons, =	60.5

On further rectification these distillates yield :—

90-per-cent. benzol.....	about 6	gallons
Solvent naphtha.....	„ 74	„
Carbolic acid	„ 6½	„
30-per-cent. anthracene	0.50	cwt.
Equal to pure anthracene	0.15	„

A. J. Dickinson gives as the average yield from 1000 gallons of London tar :—

	gallons.	per cent. by volume.
Naphtha (containing 6 per cent. benzol)	30	3
Ammoniacal water.....	30	3
Anthracene (at 25 per cent.)	10	1
Pitch	650	65
Creosote, lubricating-oils, carbolic acid.	280	28

The following table of the products of a 20-ton still, by Watson Smith*, is very instructive. The tar (from Lancashire) was of sp. gr. 1.167 at 15½° C. The still held 3672 gallons = 19½ cwt. The fractions were collected singly, one after another (except only Nos. 1 and 2, collected at the same time) :—

	gal.	sp. gr.
1. 100 first runnings.....		0.897 at 10° C.
2. 90 ammoniacal liquor (4-per-cent.)		
3. 100 light oil (including carbolic oil) .		0.932 „ 16
4. 100 light oil		0.960 „ 22
5. 100 „		0.980 „ 22
6. 100 „		0.991 „ 29
7. 100 „		1.010 „ 24
8. 100 „		1.014 „ 28
9. 100 Creosote oil		1.021 „ 28
10. 100 „		1.025 „ 23
11. 100 „		1.031 „ 24
12. 100 „		1.034 „ 25
13. 100 „		1.043 „ 25
14. 100 „		1.048 „ 22
15. 100 red oil.....		1.059 „ 24
16. 100 „		1.066 „ 30
17. 100 „		1.085 „ 33

* Private communication.

The fractions 9 to 11 on cooling yielded considerable quantities of naphthalene; the rest, beginning from 12, were put aside to crystallize for anthracene. But from fractions 12 to 14 little or nothing crystallized; only the "red oils," from 15 onwards, deposited crude anthracene on standing. By three distillations, 2·617 per cent. of the oil, or 0·35 per cent. of the tar, of crude anthracene cake were obtained from these oils.

The pitch weighed 11·48 tons; from this, again, 0·556 per cent. (=0·33 per cent. on the tar) of anthracene cake could be obtained.

From a charge of 6·2 tons of Wigan cannel-coal-tar Watson Smith obtained :—

First runnings	29 gallons, sp. gr.	0·919
Light oils	100 " "	1·000
Ditto	100 " "	1·019
Creosote oil	220 "	
Red oil	295 "	
Pitch	4 tons.	

The creosote oil was clear; and on cooling only traces of naphthalene separated; a little paraffin was also present.

He obtained the following results from Manchester tar :—

	Price in 1870.
Employed, 19·125 tons of tar.....	@ 25s. per ton.
Obtained, 11·475 " pitch.....	@ 20s. "
0·137 " crude anthracene.....	@ 1s. per lb.
1360 gal. creosote oil	@ 1d. per gal.
30 " crude carbolic acid (extra good)	@ 3s. "
149 gal. rectified solvent naphtha...	@ 1s. 6d. "
55½ " 50-per-cent. benzol	@ 2s. 6d. "
90 " ammoniacal liquor	(3 per cent.).

The materials required for distillation and purification were :—

- 10 tons of coal for the still, steam, &c.
- 14½ gallons concentrated sulphuric acid.
- 10½ " brown acid (at 140° Tw.).
- 2 cwt. 1 qr. caustic soda (60 per cent.).
- 2 to 3 cwt. quicklime.

A very recent statement in the 'Chemiker Zeitung' (1879, p. 148) puts the yield from 11250 litres (= 10 tons) of London tar at:—

50-per-cent. benzol	12.96 litres = 1.1 per cent.
Solvent naphtha.....	12.15 „ = 1.0 „
Burning naphtha	16.75 „ = 1.4 „
Creosote oils	373.5 „ = 35.0 „
Anthracene cake (30 per cent) ..	11.25 „ = 1.0 „
Pitch	5870 kilog. = 58.6 „

Crace Calvert * gives as the yield from the tar of

	Light oil.	Neutral heavy oil.	Phenol.	Paraffin.	Naphthalene.	Pitch.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Boghead	12	30	3	41	...	14
Cannel coal	9	40	14	...	15	22
Newcastle coal ...	2	12	5	...	58	23
Staffordshire coal.	5	35	9	...	22	29

(All the treatises repeat these statements without pointing out how absurd they are on the face of them. To mention only two things, how is it that all the products sum up to 100 per cent., as if tar could be distilled without any loss? and is it really credible that Newcastle tar contains only 18 per cent. liquid products, along with 58 per cent. of naphthalene and 23 of pitch?)

Lastly, we mention the statement of Häussermann (Industrie der Theerfarbstoffe, 1881, p. 13), that 100 parts of tar from German coals yield

5-8	per cent. light oil,
25-30	„ creosote oil,
8-10	„ anthracene oil,
50-55	„ pitch.

The final products are

0.6	per cent. benzene,
0.4	„ toluene,
0.5	„ higher homologues,
8-12	„ pure naphthalene,
5-6	„ phenol,
0.25-0.3	„ anthracene (pure).

* Compt. Rend. xlix. p. 262.

Testing of Tar.

If a sample of tar has to be tested for its yield on a smaller scale, its distillation must be carried on in exactly the same way as on the large scale. The result will be all the more reliable the larger the scale of the testing operation. When distilling, say, 10 gallons, the results will be only approximative, especially for benzol and naphtha. It is better to employ small stills holding 80 to 100 gallons; but it is even preferable distil 200 or 250 gallons from a light-oil still (Chapter IX.). The products are respectively weighed and measured; and light oil and naphtha are tested for their yield of benzol and naphtha according to the rules given at the close of Chap. X.

According to Watson Smith, the richest and best tar comes from small gas-works, because there the greatest possible yield of gas from the coal is not, as at the large works, such a primary consideration, and hence such high temperatures are not employed. There are contractors who drive about in the country buying up such small lots of tar and gas-liquor, and taking it to the tar-distillers for sale.

CHAPTER V.

PITCH.

WE have seen in the last chapter that the distillation leaves a more or less consistent residue, according to the way in which it has been carried on. If only the light oil is distilled off (that is, if the process ceases when the specific gravity of the distillate equals that of water), the residue remaining in the retort (about 80 per cent. of the weight of tar) is called asphalt (*brai liquide*). If 10 per cent. more is distilled off, the residue is soft pitch; next comes moderately hard pitch; and hard pitch is obtained, if the process is carried as far as wrought-iron vessels will permit (p. 123).

Asphalt thus contains all the creosote oil, *i. e.* naphthalene, phenols, and all higher-boiling substances. It is employed for keeping off the subsoil moisture from metal pipes, iron tanks, &c. sunk in the ground. For this purpose the semiliquid mass is mixed with sand, ashes, &c. into a lumpy paste, of which a thickness of 4 or 6 inches is employed. We shall quote particulars of such mixtures below.

Such asphalt, made direct from tar, is not used now so frequently as formerly; but similar mixtures are artificially made, by driving off all the creosote and anthracene oil, and pumping back the heavy oils, meanwhile freed from their more valuable components, as phenol and anthracene, till the desired consistency of the residue has been attained. Thus is obtained not merely soft pitch, but also asphalt, and, with greater dilution, even "prepared tar" or "artificial Stockholm tar," which is especially largely employed in the manufacture of roofing-felt (see below).

The employment of pitch or asphalt for *street-paving* is to be recommended in many respects. When used as a cement for

joining the paving stones, it makes the soil impermeable to the impurities from below and does not permit the passage of noxious effluvia. Tar-pitch is also used as a direct *substitute for natural asphalt* (but only in combination with the latter) for asphaltting foot-paths, and for insulating foundation walls from the ground-moisture. The mixture is melted in pans in the usual way; sand, brick-dust, ashes, chalk, and the like are added till the mass has become thick enough (for which purpose about four times the weight of the pitch will be necessary); the whole is well mixed up, and used hot. For foot-paths the pitch is ground up with an equal weight of sandy or stony material, melted in a pan, and, before being laid down, is mixed with an equal quantity of gravel; so that the finished pavement contains about 30 per cent. of pitch. But it is not advisable to employ coal-tar pitch alone, without any natural bitumen; the latter is much more intimately combined with the earthy matters than the former can be. A mixture of the two is very suitable, and is cheaper than natural asphalt alone. In a similar way, moulded blocks are made from pitch and ground rock.

Gobin (patent No. 1865, May 9, 1878) melts 15 parts of bituminous shale with 35 parts of coal-tar pitch in a pan, till the froth which at first arises has subsided. Then he adds 10 parts of coke and 130 of limestone, both crushed, well mixed, and dehydrated by heating above 100°. Before cooling he adds another 160 parts of gravel, well dried by heat. For street-pavements he increases the quantity of gravel up to 190 parts, moulds the mass into blocks of about 8 × 6 × 4 inches, and lays these, like ordinary paving-stones, on a bed of gravel or sand.

Daguzan (Germ. patent 4999) mixes tar, first completely dehydrated by heat [probably he means "asphalt"] with previously "calcined," finely ground limestone or marble (quicklime?), 5 per cent. oxide of iron, potassium silicate, calcium sulphate, &c.

Thenius * proposes mixing soft pitch with 10 per cent. of rosin oil, which is to make it more like natural asphalt, or with 50–60 per cent. of crushed limestone. This mixture is moulded into blocks, and is, with the addition of 25 per cent. of ground gravel or basalt, cast into mosaic plates for pavements, tables, &c.

Tar asphalt can be considerably improved by the addition of

* Technische Verwendung des Steinkohlentheers, p. 117 *et seq.*

brimstone. A. Winkler * adds to coal-tar asphalt (in the sense of the term adopted in this chapter) 5 per cent. of brimstone in small quantities, heating the mixture every time till no more sulphuretted hydrogen is given off. Probably, in the heating, the sulphur decomposes the components rich in hydrogen, and thus renders the residue less fusible. Thus 75 per cent. of the tar is obtained as good asphalt, which does not soften in boiling water. A further proposal of his does not seem practicable, viz. to add 20 per cent. of brimstone to the tar before distillation; it is said that in that case only water and sulphuretted hydrogen escape during the heating, and good asphalt is obtained, equal in weight to the tar employed. The expense, the action of the sulphur on the metal of the stills, and the nuisance caused by the sulphuretted hydrogen would be objections. A similar mixture is Häusler's wood-cement, well known in Germany as a roof-covering.

Coal-tar asphalt, or very soft pitch, is also employed for manufacturing *asphalt pipes*. This industry has been minutely described by Behrend †. Endless hemp paper, 7 feet wide, is passed through a semicylindrical pan set in a furnace and filled with hot pitch ‡. A roller revolving in the pan takes up the paper soaked with pitch and conveys it to a smaller roller, forming the core of the pipe, round which about 100 layers of paper are wound. When the proper thickness has been obtained, fine sand is dusted on, and the whole is exposed to considerable pressure, which increases the compactness and homogeneity of the mass. After a short cooling in water, the core (which had previously been rubbed with soft soap) is drawn out by means of a crane, and the pipe is once more cooled by water. The joints of the pipes are made by iron flanges put upon them, or by thimbles formed of a wider piece of asphalt piping, and fixed on the pipe by a mixture of pitch and brimstone, or else by winding round them ten or twelve folds of linen cloth soaked in melted pitch. Similarly any necessary elbow pieces and bends are made, often at the place where the pipes are laid down.

According to the nature of the pitch employed, the pipes have different qualities, which must be taken into account in using

* Chem. Centralblatt, 1858, p. 337.

† Dingler's Journ. cccviii. p. 377.

‡ That Behrend does not mean real pitch, but either asphalt or very soft pitch, is apparent from the fact that paper would be partially destroyed at the melting-temperature of hard pitch.

them. If made with very soft, oily pitch, the pipes offer great resistance to the penetration of water, and hence are excellent for water-pipes in marshy ground. Those made of harder pitch offer a greater resistance to deformation by a higher temperature. Of course asphalt pipes can only be employed for conveying cold liquids or gases; but, with this restriction, they can be used for many purposes, both on account of their relatively low price and their valuable qualities. They resist a pressure of 33 atmospheres from within [?], and are elastic enough for their joints not to break in case the ground settles down; they are not subject to be frozen up, being bad conductors of heat; they are not acted upon by dilute acids or alkalies, and can be laid in any soil. They are chiefly employed for conveying water, acids, air-blasts, for pit-ventilation, for covering underground telegraph-wires, for speaking-tubes, and sometimes for gas-pipes.

Another kind of pipes are made from (probably harder) pitch by mixing it with gravel and casting it in moulds. The walls of these tubes must be very thick, as they are brittle. Hence it is an improvement to surround them with a thin sheet-iron casing. In this shape they are very much employed in Paris.

When any kind of asphalt tubes are used, it must never be forgotten that these are liable to be deformed by heat.

Behrens (*loc. cit.*) also describes the manufacture of *asphalt paper* as a substitute for wax-paper. Ordinary wrapping-paper is wound off from a roller upon a heated drum, upon which a scraper is fixed. Melted pitch runs down in front of this to a depth of $1\frac{1}{2}$ inch. The paper thus covered with a thin film of asphalt runs over several rollers, and is ultimately wound round the last. Another kind of paper, consisting of a thin layer of pitch between two layers of paper, which is much used for papering damp walls, is made in a similar manner.

Proper *pitch* always contains the least volatile components of coal-tar, such as anthracene, phenanthrene, pyrene, chrysene, &c. (the properties of which have been described in the second Chapter), together with several ill-defined substances (as bitumene &c. and probably also free carbon). Behrens (*loc. cit.*) obtained from pitch, freed from all oils up to sp. gr. 1.120 by successively digesting it with benzene, carbon bisulphide, boiling benzene, and boiling alcohol, 23.54 per cent. of a black powder containing 90.836 C, 3.058 H, and 0.398 ash; when treated a little differently, the

residue yielded 91·921 C, 3·157 H, and 0·872 ash, quite similar to South-Welsh anthracite.

According to Habets*, good hard pitch consists of 75·32 per cent. C, 8·19 H, 16·06 O, 0·43 ash, and its specific gravity is 1·275–1·286.

Soft pitch is obtained, if the distillation is interrupted before driving off the anthracene, when the specific gravity of the distilling oils is about 1·090; *hard pitch*, if it is continued till the oils show sp. gr. 1·120; moderately hard pitch, if the distillation is interrupted between these two stages.

Soft pitch (<i>brai gras</i>) softens at	40°,	melts at	60°.
Moderately hard pitch	„	60°,	„ 100°.
Hard pitch (<i>brai sec</i>)	„	100°,	„ 150–200°.

A practical test is, kneading a sample between the teeth. If this can be done easily, the pitch is soft; if with more difficulty, it is moderately hard; and if it is crushed to powder it is hard. Soft pitch is more shining and black than the very hard pitch, which verges upon grey and has less lustre. Sometimes the latter is even a little porous; if it is more so, it is partly coked and cannot be used for patent fuel. The specific gravity of hard pitch is about 1·3.

Hard pitch is easily divided into flakes or lumps, which do not soften even in the sun, and can be always sent out in bulk, whether in railway-trucks or in ships. Moderately hard pitch can be sent out in bulk in railway-trucks, but not in ships, where it would coalesce into a mass. Hence the English tar-distillers regularly make hard pitch; and so do the French ones, at least in summer. Soft pitch can only be sent out in casks, and is mostly run into these direct from the tar-stills.

The manufacturers of patent fuel, especially in Belgium, greatly prefer soft pitch to hard; hence the German tar-distillers are compelled to make at most only moderately hard pitch.

When it is not feasible to soften the pitch while still liquid in the still by pumping oils in, the operation is more complicated. This case occurs when hard pitch has to be softened by the buyer to make it more suitable for the manufacture of patent fuel. For this purpose special *pitch-revivifying apparatus* have been

* Gurit, 'Steinkohlenbriquettes', p. 23.

Fig. 18.



constructed. Such an apparatus, as employed at the Blanzky coal-mines, is described in Payen's '*Précis de Chimie industrielle*,' 1878, ii. p. 919 as follows:—In fig. 18, C is an upright boiler,

6 feet in diameter, 9 ft. 2 in. high, holding about 320 cubic feet, and provided with a steam-jacket. In the centre revolves an endless screw V, surrounded by an annular casing, which is heated by steam entering at *f* and issuing at *h* into the outer jacket; the condensation-water is discharged by *r*. At the bottom are the annular grating G G (made of perforated iron plate) for retaining large pieces, the pipe S for discharging the revived pitch, and a cleaning-hole (*t*). The boiler C is surmounted by a wrought-iron chamber, D, of equal size, to receive the froth formed during the operation. Here is a manhole, T, and a gland for the passage of the screw V. The work is carried on in this way. A certain quantity of tar, creosote oil, or the like, is let into the apparatus through the pipe *k*; steam is admitted till the heat rises to 150°; the screw is made to revolve; and the pitch which is to be revived is gradually charged through the manhole T. More tar and pitch are added till the boiler contains about 9 tons of materials. The plate P prevents the pitch thrown in at T from falling upon the screw. The pitch is soon melted in the hot tar, the mixture passes through the sieve G, is lifted by the screw V, and thrown out again on the top. After eight hours all is melted and homogeneous; now the discharge-cock is opened and the revived pitch run into coolers, after which the operation can be commenced anew.

The revivification can be effected by means of creosote oil, naphthalene, or tar which is merely deprived of the light oil (=asphalt). It has been found at Blanzky that the creosote oil does not modify the agglomerating property of pitch, but merely renders the pitch more liquid; naphthalene increases the agglomerating property, but causes solidification at too low a temperature; the best of all is tar deprived of light oils, of which 10 or 20 parts are taken for 100 of pitch. [Probably the last tar-oils, deprived of anthracene, would be still better.]

Coal-tar pitch is an excellent *reducing agent*, *e. g.* for black-ash mixing, for making barium sulphide, &c., because it is nearly free from ashes, sulphur, and nitrogen; but it is mostly too expensive for this purpose.

As an agent for the manufacture of *cementation-steel* (blister-steel) it has been patented by E. J. Payne and W. Clarke (Oct. 5, 1872). It is contended that the iron will combine more quickly with the carbon from pitch than with that from any other source

The principal employment of coal-tar pitch is for making *patent fuel* (briquette) from small coal or coke. A detailed description of this industry does not come within the scope of this treatise. A number of special treatises have been written upon it, as the French one by G. Fouquoy or the German one by Gurlt (mentioned before); and the technical cyclopædias also contain a good deal of information upon this subject, of which we shall only give the outlines here.

Gurlt states the total annual production of patent fuel at 2½ millions of tons, of which quantity 1,000,000 are produced in France, 500,000 in Belgium, in England 300,000, in Germany 100,000 tons.

Good briquettes ought not to weigh above 22 lb., and possess the firmness of natural coals. To attain this, they must contain at least 5 per cent. of pitch, if very strongly pressed, or 7 to 8 per cent. if made with less pressure. They must not leave more than from 6·5 to 6·75 per cent. of ash, if intended for locomotive use, or 10 per cent. if for steamboat use. Their regular parallelepiped shape permits easy stowage in the bunkers. The loss in transit by disintegration is only 1 or 2 per cent., against 30 to 50 per cent. in the case of coals. They ought not to fall to pieces in the fire. Good patent fuel has 10 per cent. more heating-power than good steam coal; it makes much less dirt, and, if manufactured with hard pitch, less black smoke than most descriptions of coal.

The following statistics on the development of this industry are mainly based on a prize essay by Berg *. Its principal seat is in Belgium and France. In the former country there are 8 or 10, in the latter 30 works. In England there are works at Swansea, Cardiff, near London, and near Newcastle-on-Tyne †. In Germany there are only two factories. Of the different processes, that of Baroulier (adding to coal-dust some bituminous caking coal, pressing and heating in separate vessels) has not been successful, being too expensive and not yielding a product capable of bearing a long transit. Not much more successful have been a number of agglomerating substances successively proposed, such as vegetable

* Zeitschr. für Berg-, Hütten-, und Salinenwesen, 1880, p. 148.

† This is erroneous; the former patent-fuel works near the last-mentioned place were given up many years since.

and animal fats and oils, soap, gelatinous substances (glue &c.), mucilaginous decoctions of roots or whole plants, resins, magnesia cement, Carragheen moss, and wood-pulp. The only substances now in general use are coal-tar [not used now] and soft and hard pitch. Soft pitch, mostly used in France, is melted in suitable pans, and mixed with the coals in the liquid state; hard pitch, mostly used in Belgium*, is mixed with the coal in the state of powder, and the mixture softened by means of steam superheated to 300°; or else it is heated by direct fire, either in a hearth provided with a horizontal agitator (Chauselle), or in a revolving circular hearth with vertical agitator (Biérix). With this plan, 4½ per cent. of pitch are said to suffice. The coal is best if dressed, in order to free it from impurities, and then mixed with dry coal-dust to facilitate the pressing. There are presses with closed and presses with open moulds, the latter either with direct or indirect action. In Mazeline's direct-action press the steam-cylinder piston on rising forces, by means of a one-armed lever, the press-ram from below into the moulds, which are contained in a circular platform, revolving by means of a ratchet. The finished briquettes are forced out by the rams sliding along an inclined plane. The ratchet arrangement is liable to frequent breakages. In the indirectly acting machine of Middleton and Detowbay the pressure is caused by an angle-lever carried down by a weight; the finished briquette is forced out by a second angle-lever. Here also the platform is turned round by a ratchet arrangement. In the similar machine of Hanrez, the lever presses at the same time from above and below, limited by a hydraulic ram, the forcing-out is effected by an inclined plane, the revolution of the platform by a ratchet. In Durand and Marais's machine (especially adapted for smaller work) the ram is pressed into the mould by an eccentric sheave, afterwards by a similar sheave the closing-plate is removed and the briquette pushed out. Another similar machine has been constructed by Biérix.

In the case of machines with open moulds, the pressure is obtained by the friction of the mass at the conical mouth of the press. Hence they require more power than those just now

* According to information received by the author from other sources, it would seem that the opposite is the case, viz. that more hard pitch is used in France, more soft pitch in Belgium.

described, but do more work ; they are as yet employed exclusively with soft pitch *.

In the most widely used machine of this kind (Evrard's), the tubular moulds are arranged radially in a circle, so that the eccentric attached to the vertical working shaft can by turns force the rams in and out of the moulds. At every back stroke of the ram a fresh mass is forced into the mould, which by the forward stroke is pressed against the old mass, and forces this out of the open end of the mould. A similar machine, by Bouriez, permits the use of hard pitch also. Revollier's and Mazeline's machines are worked by hydraulic pressure.

Varnishes made with Pitch.

A very rational employment of coal-tar pitch is for making varnishes, for iron especially, but also for wood &c., of course all of them black. They are all made in a very simple way, by melting pitch with various products of tar-distillation, and hence require no introduction of any foreign matter. No plant is required but an open pan set in a covered place, so as to be heated from without ; but it is certainly preferable to employ a closed pan with a mechanical agitator. The melting-pan may be made of cast iron or wrought iron ; but it is best if made of the latter, because then no cracking (very dangerous in this case !) can occur. It may be an upright cylinder with convex bottom, or a horizontal boiler. For working on a large scale a mixing-apparatus like that represented in fig. 18, p. 148, is preferable.

In this pan the whole quantity of pitch to be worked up is melted along with a little of the oil to be employed, which promotes the melting of the pitch and prevents its speedy solidification. Still the temperature will rise pretty high before all the pitch is melted, and it is best to let it cool down a little, lest the oils now added should be raised to the boiling-point, which will of course most readily happen with light oil or naphtha. But the cooling must never be allowed to go so far that some part of the mass begins to solidify. Now the remainder of the oil is added quite

* The latter process is quite analogous to that of moulding bricks, the machines that work with dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies). But it is well known that the former take much more power and have a much larger output than the latter ; is the opposite really the case with patent-fuel presses ?

gradually, stirring each portion completely into the mass. From time to time a sample is taken out and cooled, to see whether the proper consistency has been attained.

The commonest kind of varnish is made in the manner just described, from pitch and creosote oil. In this case even a simpler process may be followed. The tar is distilled (if need be, in a separate small still) till the light oil has passed and heavy oil begins to pass, or till all the "middle oil" has passed over, say up to 240°. The fire is now drawn out, the still allowed to cool down a little, and the residue ("asphalt") diluted within the still itself with the necessary quantity of creosote oil, say $\frac{1}{2}$ of the weight of the pitch, after which it is run off in the liquid state. Or else the distillation is carried on to hard pitch, in order to obtain the anthracene; the heavy oil, freed from anthracene and, if possible, from naphthalene, is run in till the necessary degree of thinness is attained; and the mass is well mixed. The varnish thus obtained, in Germany known as "prepared tar" or "artificial Stockholm tar," is less valuable to the tar-distiller than raw tar, since the more valuable components, benzol, phenol, anthracene, and partly naphthalene, have been removed; on the other hand, it is much more valuable than raw tar for many purposes—as a paint, for the manufacture of roofing-felt, for roperies, &c. It penetrates much more quickly and deeply into wood, stone, &c. than raw or even boiled coal-tar, and dries much more quickly, even more so than wood-tar (real Stockholm tar). It is greatly to be recommended for alkali- and other chemical works, for painting any wood-, iron-, or stone-work needing protection against acids, chlorine, &c. Such prepared tar is especially very much to be preferred to boiled tar for painting iron (where raw tar, owing to its ammonia, is quite inadmissible), as it dries both much more quickly and without leaving cracks, and forms a good, shining coat. The drying takes from 12 to 24 hours, according to the weather. As this sort of varnish forms a pretty thick coat, it is only applicable to coarse iron-work, but is excellent for this.

11
A better kind of varnish is obtained by melting pitch with light oil in the above-described manner. For this purpose, not the light oil distilled from the tar, but the last fraction from the light-oil still, or the oil taken away from the carbolate of soda (compare Chapter VIII.) is employed, which is deprived of its more valuable components. For 100 parts of moderately hard pitch about 60

parts of light oil may be calculated. This varnish gives a more lustrous and smooth surface than the former, and leaves a much thinner coat. Its drying-time varies from four to six hours; and it can be employed for finer ironwork.

Lastly, more quickly-drying and thinner varnishes can be obtained in all gradations, by substituting naphtha for part of the light oil, either the commonest burning-naphtha being employed or else some made on purpose by carrying on the rectification by steam (Chap. X.) beyond the usual termination. The rule is, first to work up all the light oil with the pitch, and then to add the naphtha, keeping the mixture as hot as is consistent with the volatility of the naphtha. Besides, very thorough and long-continued stirring is necessary, since naphtha is not so easily incorporated with the varnish as the heavier oils, and the varnish would otherwise be very likely to separate into a black deposit and naphtha floating on the top of it. It is possible by means of very common naphtha to make varnishes drying in an hour, or even in a quarter of an hour, which can be employed for any kind of hardware where its blackness is of no consequence. In lieu of coal-tar naphtha, petroleum spirit &c. can be employed.

All three kinds of varnish adhere firmly to iron, and after drying exhibit a considerable degree of hardness, together with glossy lustre and smoothness, and more of the latter in the case of the better descriptions.

A patent of Marchisis and Stevens (23rd Sept. 1870) seeks to improve such varnishes by heating with bleaching-powder or a solution of common salt, and washing with copperas solution. Whether this does any good we cannot tell.

Chaumont* makes a varnish for wood and metals by dissolving 300 parts of coal-tar asphalt in 100 carbon bisulphide. In lieu of such asphalt, natural bitumen or resin may be employed. The materials are brought together in a closed vessel, to prevent the evaporation of the carbon bisulphide. In 12 to 24 hours the varnish (the smell of which will hardly recommend it) is ready for use.

Watson Smith† recommends as a good varnish for tarpaulins one obtained by melting wood-tar pitch with the same weight of coal-tar creosote oil; also as a good metal-varnish one obtained by melting

* Wagner's Jahresb. 1865, p. 686.

† Private communication.

6 lb. of dark rosin with a pint of boiled linseed-oil and a gallon of creosote oil, to be mixed, for finer work, with a little gum and any kind of colouring matters.

The Distillation of Pitch.

Long before the technical importance of anthracene had been recognized, attempts had been made to obtain further products from the pitch left behind after the distillation of coal-tar. The occasion for those attempts was the fact that coal-tar pitch was not consumed in any large quantity, except for patent fuel, and that with only this single opening the sale of the article would be very liable to stoppage. The idea of carrying on the distillation till all the volatile products were given off and only coke remained (for which there was always a certain sale) was very plausible. The motive for doing so became much stronger as soon as the discovery of artificial alizarine had raised anthracene to the rank of the most valuable component of coal-tar. It was known that the pitch contains much anthracene; and the hope of obtaining it therefrom at a profit seemed justified.

The apparently simplest plan, that of carrying on the process in the tar-still itself to the stage of coke is not feasible. We have seen on p. 92 that cast-iron is not well adapted for tar-distilling, and wrought iron would be burnt too quickly. Moreover, cutting out the coke would be very costly and would enormously injure the iron plates. A method proposed by Puls (patented August 23, 1858, No. 1910), viz. adding earthy substances to the tar, so as to prevent the red-hot residue from adhering to the still, would cause the loss of the coke, and is not worthy of serious consideration.

Hence distilling the tar up to pitch in the ordinary stills, and distilling the pitch in separate vessels, either charging them with it in the solid state, or running it while still liquid into the pitch-oven, cannot be avoided. This may be a brickwork muffle, or a fire-clay gas-retort, or an iron vessel of some shape or other.

The *brick pitch-ovens* which were formerly sometimes employed*, will be but briefly mentioned here, as they have not proved practically successful. They were muffle furnaces, about 15 feet long,

* Figured and described in Ronald and Richardson's 'Chemical Technology,' i. p. 541.

6 feet wide, and 6 feet high to the crown of the arch, fired by zigzag flues running underneath the concave-shaped furnace-bed. At each gable-end there was a working-hole, about halfway up, closed during the process. The vapours were carried away by a cast-iron pipe, 90 feet long, and were condensed by air-cooling. Usually two ovens were built side by side, each was charged with 2 tons of pitch, the doors closed with metal plates fastened like gas-retort-covers and screwed down. The fire having been lighted previously, volatile products were soon formed, which were condensed in the cooling-pipe and collected in a tank. The oil first coming over resembled the last distillates from coal-tar; the following portions were more viscid, very dark and empyreumatic. After about twelve hours when the distillation was nearly finished, large quantities of heavy yellow vapours appeared, condensing partly to a very thick pasty mass; sometimes they yielded a reddish-yellow pulverulent substance, which, on exposure to the air, soon turned soft and sticky, and contained much pyrene, chrysene, and other hydrocarbons. When nothing more came over, the two gable-end doors were cautiously opened; the vapours inside the muffle took fire, and the soot adhering to the sides and the arch was burnt. The dense smoke then issuing from the doors was aspirated by a vapour-hood and conveyed to a chimney. The cold current of air caused the layer of coke on the furnace-bed to crack and break up into pieces, the attendant using iron tools to accelerate the process. The coke was drawn out red-hot, and quenched with water. It was quite honeycombed, owing to the escape of vapours from the pasty mass. The heat produced by the burning of the soot kept the oven red-hot and caused very little fuel to be used for the next operation. One hundred parts of pitch yielded 25 parts of oil, which could be mixed with the creosote oil or sold as a common lubricant, and 50 parts of coke; 25 parts were lost. But these were *maximum* yields; in practice very much pitch was lost by leaking through the brickwork, and hence the yield was smaller than from the iron retorts.

Of newer statements upon this subject, dating since the invention of alizarine, we shall first quote a report made by Behrens*, upon experiments made by him on a large scale. He employed a cast-iron retort in the shape of a horizontal box 13 feet long, 3

* Dingler's Journal, ccviii. p. 371.

feet 8 inches wide, and 3 feet 8 inches high, constructed of 16 flanged plates, bolted together and joined by rust cement. The front and back openings were closed by iron doors, and luted with lime putty. On the top of the retort there was a manhole for charging with solid pitch, and a cock for charging with liquid pitch, and also a safety-valve and a 6-inch pipe for the vapours. The latter was connected with an iron box provided below with a swan-neck pipe to run off any liquid, and on the top with a pipe for carrying away steam and uncondensed vapours into a condensing worm. The retort was set on a flat arch, which was levelled above and heated from below by a fireplace in front; at the back the flame divided into two parts, returned, through two lower flues on each side of the retort, to the front, and once more, through two upper side flues, to the back. At first a little water comes over, especially with damp pitch; and hence cautious firing is necessary to prevent boiling over. But as soon as the pitch is fairly boiling, oily matters condense, and the distillation goes on rapidly even with moderate firing, so that 3 tons of pitch can be distilled in 3 or 4 hours and yield 14 or 15 cwt. of oils. The latter are condensed in two fractions—the first as anthracene oil, the second as lubricating-oils. From the beginning, with these arrive water, gases (especially ammonia* and hydrogen), benzene, naphthalene, and volatile oils (of sp. gr. 0.97). When two thirds of the oil have distilled, the formation of coke commences; the mass swells; and if the retort has been fully charged, the fire must now be slackened.

When the production of oil is near its close, the more volatile hydrocarbons decrease, but there is even more steam and gases. At last there comes a reddish-yellow resinous sublimate, which gradually ceases; and the evolution of gases ceases also. The retort is now carefully opened, and the gas issuing from it is lighted; otherwise the access of air might cause an explosion. There were obtained:—

Oils containing anthracene.....	} 27-30 per cent.
„ „ chrysene and pyrene.....	
Sublimed reddish-yellow rosin	
Coke	48-52 „ „
Gases, steam, and 0.2 per cent. light oils ...	25-28 „ „

* Watson Smith also has observed the evolution of ammonia in the coking of pitch.

The crude anthracene oil, on treatment with alkalis, yielded 3 per cent. of an oil soluble in alkalis, and separated again by sulphuric acid, which on distillation gave 8 per cent. of water, then more and more viscid oils, and, above 360°, a transparent wine-coloured solid mass; a little carbon remained behind.

The following apparatus of Fenner and Versmann for coking pitch has been worked on a large scale. The tar is first distilled in an ordinary wrought-iron still; that shown here (A, fig. 19) is shaped like a horizontal boiler. B is the condenser for light oils and creosote oil. When the anthracene oil is about to come over, the liquid pitch is run, while still hot, into a series of cast-iron vessels C C C, in which the coking is effected. It passes through the cock *c*, the main pipe D, and the taps *d d*, into each of the pitch-stills. Figs. 20 and 21 give details of the latter. They are made of cast iron, and are about 4 feet in diameter, and 4 feet 8 inches deep (inside measurement); it is alleged that, when set in the way indicated in the diagram, they will last five or six years, distilling off one charge of 1½ to 2 tons of pitch every three days—one day being occupied in the distillation, and two more in the cooling, emptying, and recharging. A production of 10 tons of pitch per day therefore requires three sets of six cast-iron pots each for the coking-operation. *a* is the cast-iron pitch-still; *b*, furnace; *c c c c*, flues; *d*, pitch-delivery pipes; *d'*, stop-cock; *e*, condensing-tube for the vapours evolved; *e' e' e'*, branch pipes delivering condensed liquors to the tank; *f*, condensing-chamber; *g*, tank.

The vapours evolved are condensed solely by atmospheric cooling, partly in the tube *e*, partly in the condensing-chamber *f*. The evolution of vapours is greatly facilitated by creating a partial vacuum in the pot *a* by means of an exhauster or blower attached to the exit-pipe of the chamber *f*; but no advantage is derived by blowing either hot air or steam through the pitch (compare p. 126). Towards the latter part of the distillation the branch tubes *e'*, *e'*, *e'* are successively opened, so as to provide as short and ready a passage as possible for the escape of the condensed substances into the tank *g*. This is essential; otherwise the vapour-delivery-pipe *e* is apt to become blocked up by the separation of solid matter.

The distillate of 315–370° C. is, according to Fenner and Versmann, very rich in anthracene, but little naphthalene or chrysene being therein; between 260° and 315° the naphthalene

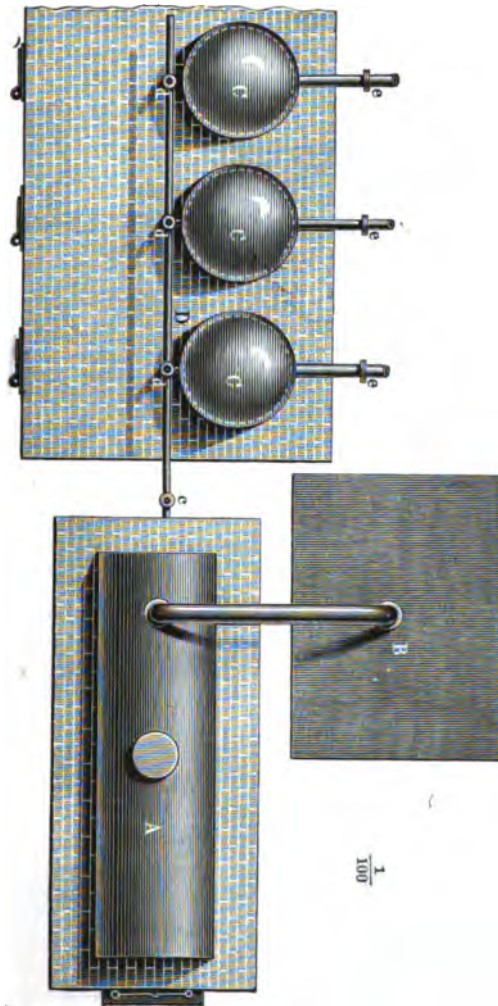


Fig. 19.

is in excess; above 370° anthracene is less abundant, chrysene and other bodies of higher boiling-point than anthracene being the main constituents of the distillate. On standing, these distillates deposit solid matter, from which rough anthracene is separated by filtration, washing with lighter oils, and pressing, as will be described in the next chapter.

Fig. 20.

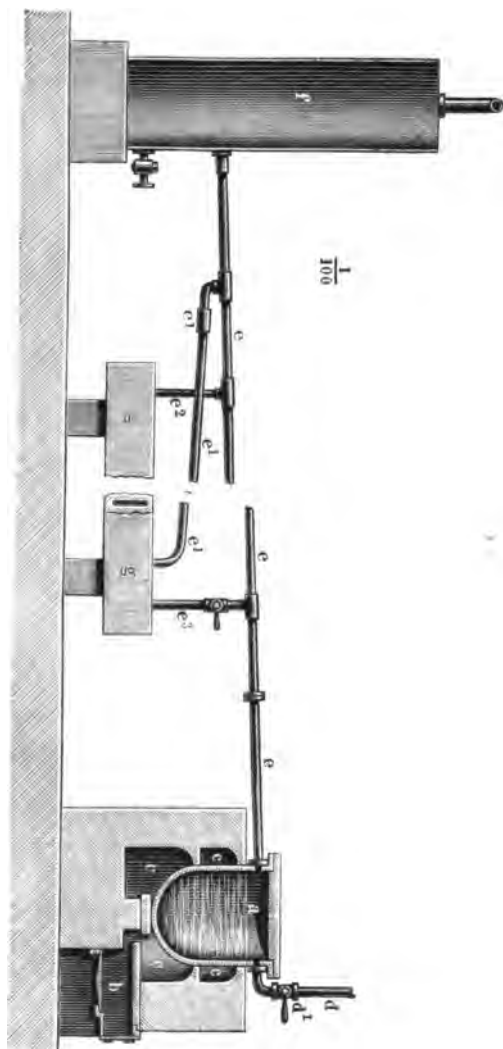


Fig. 21.



This plant may also be used for the distillation of pitch purchased in that state for the extraction of anthracene from it. For this

purpose the pitch is broken up into small lumps and, preferably, mixed with oils arising from a previous distillation, or with dry absorbent carbonaceous matter. The object of this is to prevent frothing and the blocking-up of the vapour-delivery tubes on first heating, owing to the presence of moisture in the pitch. The patentees state that, on an average, 2 per cent. of anthracene is thus obtainable from ordinary pitch. As ordinary coal-tar yields about 0.5 per cent. of rough anthracene, and 87 per cent. of pitch (this latter corresponding to 1.33 anthracene per 100 of original tar), it follows that the production of anthracene is nearly quadrupled when the tar is coked; *i. e.*, all together, 1.85 per cent. is obtained instead of 0.5 per cent. if the above statement be correct. Unfortunately "pitch-anthracene" has been found so much contaminated with chrysene &c. that the alizarine-manufacturers cannot very well purify it, and will not work it. Several lawsuits have arisen from this circumstance. The coke left behind is very good (see below); and the oil from which the anthracene is separated is a good lubricator; this is actually the only opening for the pitch-oils in general, until some better method of purifying the pitch-anthracene be discovered.

Watson Smith* obtained from ordinary hard pitch by distilling, mixing the distillate with mother oils and redistilling, no more than 0.556 per cent. rough anthracene from the pitch, or 0.33 from the tar.

The proposal of E. Kopp (p. 123) might be referred to this chapter also.

The *coke* obtained by distilling pitch is very good, if properly made, but only in that case. This matter has been treated in detail by Behrens (*loc. cit.*). The quality of the coke depends upon the temperature at which it has been made, and upon the length of time during which it has been exposed to that temperature. If both are insufficient, a dull, blackish, compact mass with but few cracks is obtained. On opening the retort this coke takes fire and burns with a luminous flame issuing through the cracks of the mass. Even though the coking is somewhat promoted by such burning out, and the cracks are widened with a crow-bar, the quality of the product is very inferior, owing to all pitch-coke, except the very hard-burnt kind, crumbling to dust in the fire. Hence coke that

* Private communication.

is only burnt out afterwards, possesses but very little cohesion; and as it strongly adheres to the sides of the retort, much dust is already produced in breaking it up and getting it out. Coke not ignited, having been quenched with water, must from time to time be drenched with water again, as otherwise it easily breaks out into a flame. In order to make *hard* coke, the temperature inside the retort, when the red vapours indicating the end of the distillation have disappeared, must be brought to a bright red heat; and this should be kept up for eight hours at least. Thus a complete operation lasts about 24 hours. Hard-burnt coke adheres but little to the sides of the retort, possesses great cohesion, and consists of prismatic-columnar pieces, which can be got out of the retort almost without using a crowbar. After being once quenched it does not take fire again. It is light grey, very dense, and does not crumble in the fire. Behrens made some experiments with such coke in English iron-works, with the following results. No success was attained in employing it for melting cast iron in cupolas, in lieu of charcoal, or for refining wrought iron on hearths; in the latter case the slag was not easily separated from the iron. But hard pitch-coke is very good for refining pig-iron in the English way, which is usually done by gas-coke; the refined pig afterwards yielded very good wrought iron on puddling. That coke is also very well adapted for fusion processes in crucibles.

According to Staveley*, pitch-coke contains only 0.11–0.12 per cent. sulphur and 2.43–2.50 per cent. ashes; it does not crumble even when exposed for months in the open air, as there is no sulphide of iron in it; and it surpasses even the best Durham coke in hardness, density, heating-power, and strength to sustain heavy loads.

A principal difficulty in the distillation of coal-tar pitch, which prevents this operation from being very extensively carried out, is that of finding a suitable material for the retorts. Brick muffle furnaces leak too much; fireclay retorts require too much fuel in proportion to the quantity of pitch worked up; cast iron is quickly destroyed by the heat and the pitch, although Fenner and Versmann assert the contrary respecting their construction figured above.

Cyrus M. Warren (German patent No. 12933, July 16, 1880) proposes distilling tar as usual down to hard pitch, then running

* Chem. News, xliii. p. 228.

into the still, whilst hot, residues from petroleum-refining, and distilling off once more as much of oils as corresponds to the weight of the petroleum-residues. From this oil anthracene separates, together with paraffin, which latter is removed by hot-pressing. (It is doubtful whether this plan will furnish very much saleable anthracene.)

More rational would appear the proposal of Wischin (Engl. pat. 1980, 1880), to add gradually, at the last stage of tar-distillation, heavy coal-tar oil, preferably heated beforehand, whose vapours carry away the anthracene without injuring the quality of the pitch.

A proposal made by Behrens (*loc. cit.*) to employ the pitch in *gas-making*, by melting it and running it through a bright-red iron tube, yielded, on an average, for 1 kilog. pitch, 250 litres of gas, but almost devoid of illuminating-power. It consists mainly of hydrogen, and contains some sulphur.

When pitch cannot be utilized in any other manner, it can be *burned to lampblack*. The furnaces and condensing-chambers for this purpose are similar to those described on p. 81 for burning tar. Only, as the pitch is solid, it must from time to time be thrown upon the red-hot iron plates on which it is to be burnt. No doubt a vessel might be fixed above this, where the pitch would be melted by the combustion going on below, and from which it would be run out continuously by means of a valve in the bottom. According to Thenius 500 kilog. of pitch yield 200 of different descriptions of lamp-black, and 200 kilog. of coky residue, which is knocked off with hammer and crowbar, and used as fuel. Along with pitch any dry alkaline residues from purifying the tar-oils may be burned; but usually there are none such obtained, as the alkali is employed in aqueous solution.

CHAPTER VI.

ANTHRACENE OIL.

ANTHRACENE OIL (green oil, green grease, red oil) consists of the highest-boiling portions of coal-tar, starting from the point at which the oils begin to separate solids again (*i. e.* when the thermometer shows about 270° C. in the vapour) to the end of the distillation. It contains essentially the following bodies—naphthalene, methylnaphthalene, anthracene, phenanthrene, acenaphthene, diphenyl, methylanthracene, pyrene, chrysene, retene, fluorene, fluoranthene, chrysogene, benzerythrene, carbazol, acridine; but along with these hydrocarbons, all of which (except methylnaphthalene) are solid and partly only fuse at a high temperature, there is a mixture of liquid, high-boiling oils of which we know as yet next to nothing. The whole forms a mass rather thinner than butter, with crystalline grains or scales mixed in, of greenish-yellow colour.

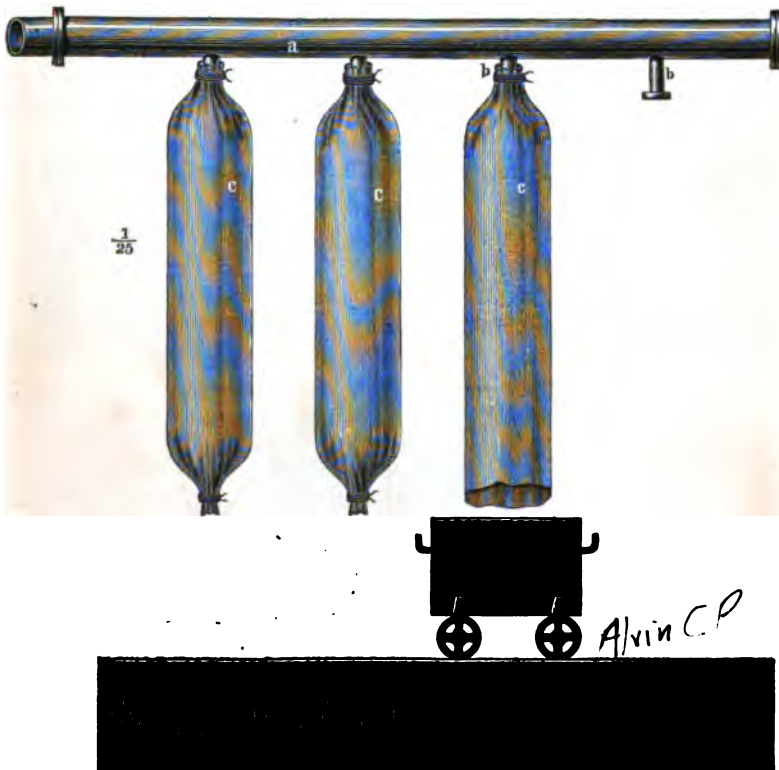
The working-up of anthracene oil consists essentially in the separation of the solid hydrocarbons from the liquid ones by cooling and pressing. The latter go back to the heavy oil, of which the anthracene oil was the last fraction; or they are employed as lubricants, or are redistilled. The solid portion is either sold as rough anthracene or is further purified by “washing.”

Simple as the process of making rough anthracene looks, the different ways in which it is carried out make great differences in the yields of anthracene, which, from the high price of this article (3*s.* or 4*s.* per pound), very much affect the profits of tar-distilling.

The anthracene oils are sometimes separated in two fractions, apparently without much advantage. They are first allowed to

rest for some time, so as to cool and deposit the crystallizable substances. Even in summer three to five days should suffice; but at some works a fortnight is allowed. In any case much anthracene remains dissolved in the liquid oils, which are therefore often redistilled in order to obtain more. Possibly cooling by means of refrigerating machines would hasten and complete the crystallization; but as it also renders the mother oils very viscid, artificial cooling would seem adapted only for the hot season. The cooling is best done in shallow iron pans, not above 18 inches deep; where space is an object, several such may be mounted on the top of one another.

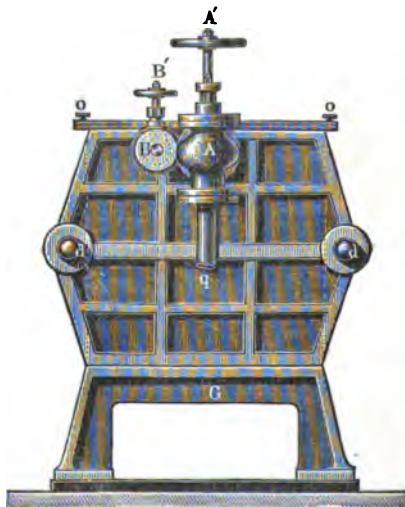
Fig. 22.



When the crystallization is complete, the pasty mass is forced by air-pressure into filters made of strong bagging. Even in this there are differences; and at some even very large works long

rows of bag filters of the old shape are found, in which the oil slowly drains off. Much better is the following plan, often followed by English tar-distillers, the apparatus forming a rough kind of filter press. A force-pump, or compressed air, forces the paste into a 4-inch main pipe *a* (fig. 22), from which branch off a number of 1-inch T-pieces *b b*. Over their flanged ends sacks, *c c*, made of strong bagging, are tied with string. The sacks are open below, but are at first tied up there also. When filled they are about 1 foot in diameter and 4 or 5 feet long. They hang over a tank for receiving the oil draining off. When the forcing apparatus is set in motion, the sacks are filled with the anthracene-oil paste, of which the liquid portion at once begins to drain off. This goes on slowly, as the oils are viscid; but by increasing the pressure, until the gauge shows at last 1 atmosphere over-pressure, the draining is made much more speedy and complete, so that the contents of the sacks become nearly dry. Certainly some considerable quantity of the finer crystals is forced through the bagging along with the oils; therefore the latter must be allowed to settle, and the deposit

Fig. 23.

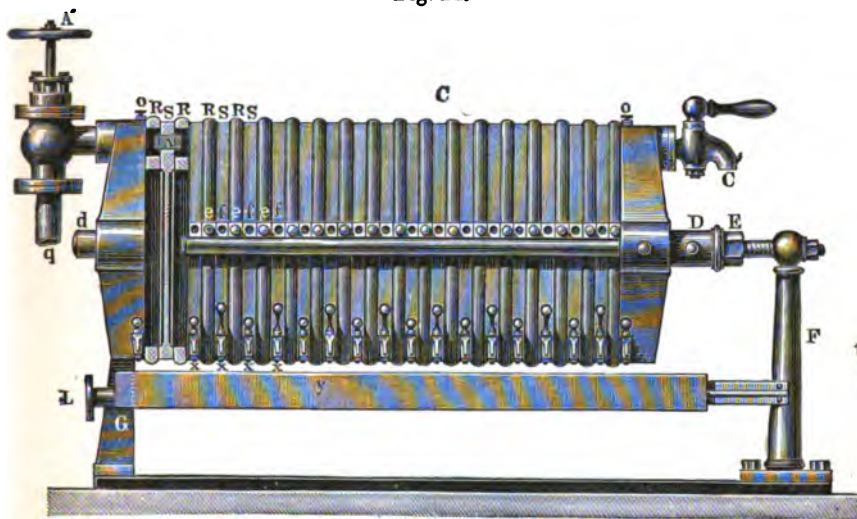


must be pressed again. When, in spite of pressure, nothing more runs out, the sacks are emptied. For this purpose a small carriage

d, is run on a line of rails underneath each sack in turn; the lower string is untied, and the falling-out of the contents assisted by knocking upon the sack. The rough anthracene thus obtained usually contains 12, or at most 15, per cent. anthracene by Luck's test.

Much more thorough and cleanly is the action of *filter presses*,

Fig. 24.



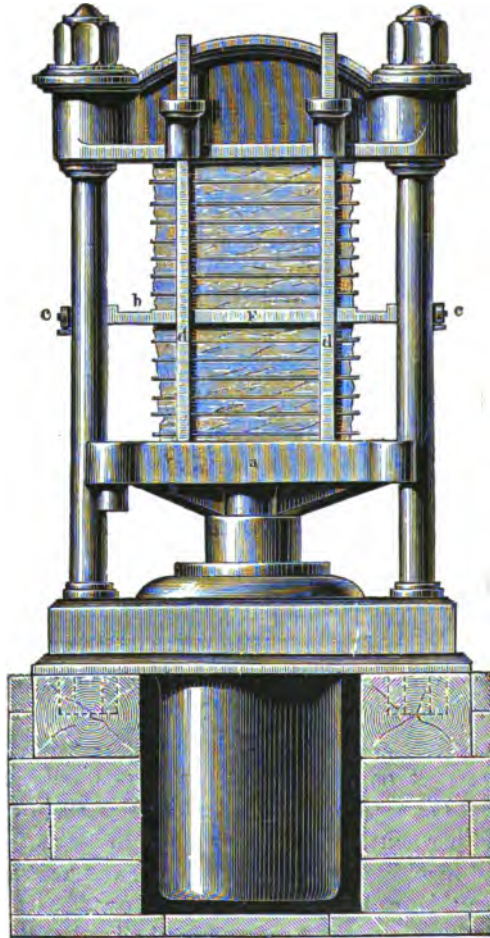
of which there is now quite a number of systems. That of Danek (manufactured by Dehne, at Halle) is represented in figs. 23 and 24. It seems unnecessary to give here details about the construction and treatment of filter presses, always obtainable from the makers. The German works visited by the author did not get more than 12 per cent. anthracene even with them.

Centrifugal machines are also employed, and are said to answer, especially for thicker oils. At a German works it was asserted that 16 or 17 per cent. anthracene was obtained with these, which is not easy to understand, since usually presses act better than centrifugal machines.

Now follows in any case pressing the product by *hydraulic presses*, either vertical or horizontal. Vertical presses (fig. 25) are most usual; they are just like those employed at beetroot-sugar works. The rough anthracene is put into cloths and so exposed to

a gradually rising pressure, at last up to 300 atmospheres, till nothing more runs off. Sometimes, especially if the first draining

Fig. 25.



has been effected in bag filters only, the first pressing is done cold ; and at one of the works visited by the author they asserted that they got up to 30 or 32 per cent. anthracene by mere cold pressing. But mostly that strength is only attained by heating the oils, to make them more liquid and to melt the naphthalene. The application of heat takes place in various ways. Sometimes the oil is warmed

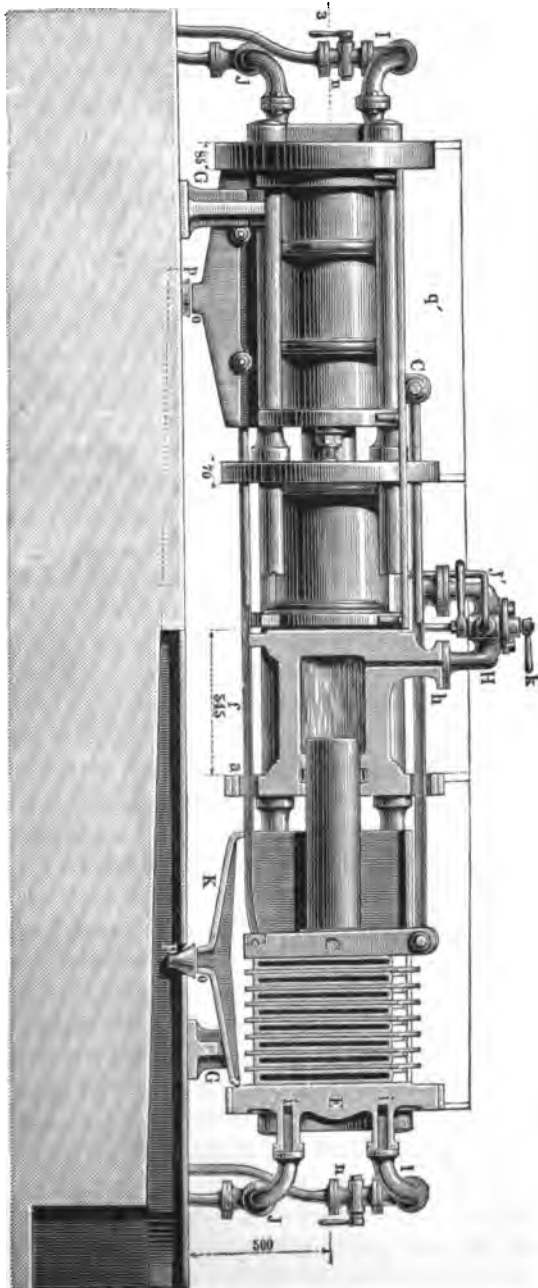


Fig. 26.

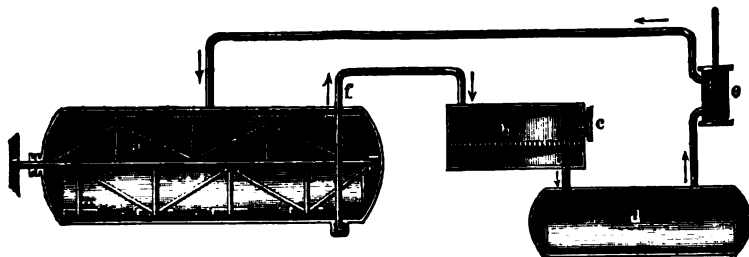
before pressing, in a pan with double bottom, by means of steam, and is then pressed in an ordinary hydraulic press. This process will hardly yield such uniform results as real hot pressing, especially in winter. In England the presses are surrounded by a wooden jacket, and steam is passed in during this operation. This process is not very cleanly; and the redistillation of the pressed oils is made more troublesome by the admixture of liquefied steam. Far the best, although more costly to erect, are *horizontal* presses like those used in the stearine-manufacture (fig. 26), whose hollow plates are heated by steam. Whilst with the English presses, heated by a steam-jacket, the manufacturers themselves only claim getting 35 or 36, or at most 38 per cent. anthracene in summer, and sometimes only 23 or 25 per cent. in winter, at the above-mentioned German works, where a filter press turns out 12 per cent., and the cold hydraulic press up to 32 per cent. anthracene, the horizontal hydraulic press with plates heated by steam yields 50 or even 52 per cent. anthracene, without any washing with naphtha.

As a rule such rich anthracene is only got by *washing*, *i. e.* treating with solvents of the impurities. As such, carbon bisulphide and alcohol have been thought of, but have hardly ever been employed, on account of their cost, their volatility, and the danger of fire. Very generally the "solvent naphtha" which is got on rectifying the light tar-oils, and essentially consists of xylenes, pseudocumene, and mesitylene, is employed. It distils between 120° and 190°, as we shall see in detail in Chapter X. In this naphtha especially phenanthrene is much more soluble than anthracene. In England petroleum spirit of not more than 90° boiling-point is frequently used; that boiling at 100° dissolves too much anthracene.

Before washing, the rough anthracene cake must be ground up into fine powder, which must also be done for sale. The grinding is done by any sort of machine, such as horizontal mills, edge-runners, studded rollers, Carr's disintegrators, &c. The powder is usually stirred up with the naphtha in tight iron boilers, vertical or horizontal, fitted with a mechanical agitator and with a steam-jacket or an interior steam-coil. This is done for several hours, gentle heat being applied; and the whole is then forced by compressed air into a filter, consisting of an iron box with an inner perforated false bottom, covered with canvas, where the solution is separated from the solid parts, the separation being much aided by

the air-pressure. To avoid danger of fire, the filters, the tanks for receiving the oils, &c. must not communicate with the outer air. It would seem advisable to employ an arrangement sketched in fig. 27: *a* is the dissolving-boiler with its agitator; *b*, the filter, with

Fig. 27.



the man-hole *c* for removing the anthracene; *d*, the vessel for receiving the solution of the impurities in naphtha; *e*, an air-pump, aspirating the air from *d* and forcing it into *a*. Thus the whole of the paste is forced through the pipe *f* into the filter *b*, and the solution through it into *d*. In this way there is always the same quantity of air circulating, and a loss of naphtha is avoided as much as possible. Or else the mass may be treated in a centrifugal machine. The *once-used naphtha* is always recovered, except the inevitable loss, by distilling the solution. The *residue* remaining in the still, consisting mainly of phenanthrene, along with some naphthalene, phenol, and unknown liquid lubricating-oils, does not, up to the present, appear to be used for any thing except burning to make lampblack (p. 81), for which it is very suitable; but care must be taken that no water remains mixed with it.

Owing to the great danger of fire, the washing of anthracene and the recovery of the naphtha ought to be performed at some distance from the other erections, and not in very large apparatus.

The washing with naphtha yields a product of at least 48 or 50, and with proper care upwards of 50 per cent.; the highest *reliable* amount given is 70 per cent., and refers to the above-mentioned article that had been previously brought to 50 per cent. by three pressings. On the other hand, some makers only get at most 30 or 40 per cent., by treating the rough anthracene, merely purified in the centrifugal machine or filter press, with naphtha and then

submitting it to hydraulic pressure. Hence the former process seems more rational than the latter.

At one of the largest English works they wash first with *crude* solvent naphtha (*i. e.* the second distillate of the light-oil still); they are said to get as much as 56 or 60 per cent. in this way.

Perkin * prefers washing with petroleum spirit, boiling between 70° and 100° C., which dissolves less anthracene than coal-tar oils, and yet removes the impurities sufficiently. Coal-naphtha sometimes dissolves 7 or 8 per cent. by weight of anthracene, which is difficult to recover. Carbazol is not removed by any solvent. The following table shows the solubilities of anthracene and some other bodies:—

	Petroleum spirit. B.p. 70–100°.	Benzol. B.p. 80–100°.
Anthracene.....	0·115	0·976 per cent.
Phenanthrene.....	3·206	21·94 „
Carbazol.....	0·016	0·51 „
Dichloranthracene	0·137	0·52 „
Anthraquinone ...	0·013	0·166 „

A most disagreeable impurity in anthracene is *paraffin*, which differs from ordinary paraffin by fusing at a much higher temperature, and is little soluble in either petroleum spirit or naphtha. But little of it suffices for disturbing the filtrations necessary in the subsequent operations; it resists pretty completely all the chemical processes to which anthracene and anthraquinone are subjected.

The purification of anthracene by washing is frequently carried out, not at the tar-works, but by special anthracene-refiners, or at the alizarine-works. The latter does not seem very rational—first because this operation is much more in the style of tar-distilling than in that of colour-making, involving as it does the danger of contamination and of fire for those expensive products, secondly because the tar-distiller can manufacture and recover the naphtha more cheaply than the colour-manufacturer.

A peculiar anthracene-purifying process was carried out for some time at the English alizarine-works, and communicated under the seal of deep secrecy to one of the largest German works. The

* Wagner's Jahresh. 1879, p. 1068.

secret was even kept for years after the process had been proved to be unsuitable and had been given up. It is now known what it consisted in*. Anthracene is mixed with *caustic potash* and a little lime, and is distilled out of cast-iron gas-retorts. These are connected by iron elbow tubes with shallow iron boxes, in which the distilling anthracene condenses without further cooling. The covers of these boxes are put on loosely, so that the gases evolved at the same time can escape, and can even take fire without doing any harm. Caustic soda cannot be employed, because its fusing-point is too high; and as that of caustic potash is too low, quicklime is added. 200 kilog. of anthracene are ground up with 60 kilog. Montreal potash and 12 kilog. quicklime, during which operation the smell of ammonia is often perceived. The mixture is distilled at a low red heat. When this mass is diluted with water, a green solution is obtained which deposits greenish-blue flocks of extremely disagreeable smell. After the distillation the retort contains a porous, wax-like substance which takes fire on contact with air and deposits a sublimate of carbazol in the cooler parts. In fact this body was discovered by Graebe and Glaser on this occasion, and does not seem to be easily obtainable in any other way. The distillate forms solid yellow pieces, containing about 40 per cent. real anthracene. From the residue in the retorts the caustic potash can be recovered by dilution with water and boiling with lime. The distillation with caustic potash is said to destroy the chrysene; but the destruction seems to extend to the anthracene, as shown by the following figures:—600 kilog. of 31-per-cent. anthracene cake were distilled with 180 kilog. caustic potash and 36 kilog. lime; the result was 380 kilog. 44-per-cent. anthracene, equal to a loss of $17\frac{1}{2}$ kilog., or 10 per cent. When the considerable quantity of fuel for heating, and the considerable wear and tear of the retorts are considered, it becomes apparent that this process is much too costly. But the anthracene purified in this manner is the best material for preparing chemically pure anthracene; compare p. 51 (Auerbach, *loc. cit.*).

It is sometimes asserted that pitch-anthracene suffers a considerable loss in this operation, but tar-anthracene none at all (?).

Perkin (*loc. cit.*) states that in this process no more anthracene is lost than in distilling without potash, but 40 or 50 per cent. of the impurities are removed. The phenols are retained in the

* Auerbach, 'Das Anthracen,' 2nd ed. p. 11; Perkin, *loc. cit.*

residue*, also a non-volatile compound of carbazol, of which sometimes as much as 10 or 12 per cent. occurs in crude anthracene; so that the distillate consists essentially of anthracene and phenanthrene. The alkaline process is indispensable for the manufacture of alizarine by means of dichloranthracene; and all crude anthracenes, even the worst, yield the same good quality. Anthracene, washed before distillation with naphtha and petroleum spirit, yields again after distillation a considerable amount of impurities to those solvents (probably phenanthrene). If the process possessed all these advantages not counterbalanced by any drawbacks, it is difficult to understand why it has been given up again.

C. Caspers† proposes the following purifying process. Well-pressed anthracene cake is mixed at from 12° to 15° C. with its own weight of paraffin oil, which dissolves naphthalene, phenol, cresol, &c. The residue is washed several times with paraffin oil (always at or below 15°), and last of all with methylated spirit, pressed, and dried at 100°. The product is said to contain 85 or 90 per cent. of anthracene fusing at 190°. This can be further purified by fusing and heating to 205°, when a dark green crystalline mass is formed, containing 95–97 per cent. anthracene, and yielding perfectly pure anthracene by sublimation (?). If the crude anthracene contains higher-fusing bodies, as pyrene, chrysene, &c., the washing with paraffin oil is carried on at such a temperature that the anthracene is dissolved, whilst chrysene &c. remain behind; on cooling the clear solution down to 15° the anthracene separates and is purified as above. (The author is not aware that this process has anywhere been adopted.)

P. Curie‡ asserts that a larger yield of anthracene is obtained by adding sulphur to the tar-oils before distilling. A copious evolution of sulphuretted hydrogen takes place.

The *oils draining from rough anthracene* in the presses &c. are sometimes added to the creosote oil sent out for pickling wood; sometimes they are sold at a higher price as lubricators. It is most rational to distil them once more in ordinary tar-stills, to recover more anthracene, which no doubt previously existed in the oils, but has been kept dissolved by the liquid components, and hence can only be obtained (no doubt only partially) by a new

* This seems doubtful. It is well known that the compounds of phenol with potassium or sodium are partially split up by heating into free phenol and alkali.

† Patent, May 9, 1873; Chem. News, xxxix. p. 166.

‡ Chem. News, xxxi. p. 175.

fractionating. In other places the oils are only kept for several months, and the newly formed deposit is collected. E. F. R. Lucas * runs the tar-oil that distils between 260° and 360° (undoubtedly after separating the anthracene) through red-hot tubes filled with bricks, and distils the dark oil formed thereby; the oil distilling at 360° is rough anthracene. Almost the same proposal has been patented once more by Hardman and Wischin (No. 4517, Nov. 7, 1878), who substitute coke for bricks.

A. M. Graham † describes the following process as the most suitable, from practical experience on the large scale, for extracting the anthracene from the filtered oils, which are frequently allowed to accumulate to an inconvenient degree because the anthracene obtained from them is generally so impure as to be unsaleable. Fractional distillation, retaining only that portion of the distillate which comes over between 300° and 360° , is difficult and expensive. He prefers distilling, say, 1500 gallons of the filtered oil in a perfectly clean tar-still, free from tar and pitch, until crystals of anthracene begin to appear in the distillate on cooling. The distillation is then stopped; and after the temperature of the remainder has been sufficiently reduced, it is run out into a tank and allowed to cool, when the anthracene crystallizes out in large quantity. A second and a third operation can be performed in this way; but usually it is found that the oil is sufficiently exhausted in one operation. The solid portion deposited in the tank will be found, after filtering and pressing, to contain at least 17 per cent. of real anthracene; and this can be easily raised to 36 per cent. by fractional distillation or by washing.

Watson Smith ‡ was able to recover from the pressed oils, after treating them, hot, with a little concentrated sulphuric acid and caustic alkali, a large quantity of anthracene by repeated distillations. The last oil boiled at 260 – 290° ; the fraction distilling between 260° and 280° remained quite colourless after long standing; it had a pleasant, hay-like smell, and the sp. gr. 1.04. It is miscible with paraffin oil and animal oils, and dissolves a considerable amount of tallow. It is also by itself a good lubricant. He could also isolate 0.28–0.45 per cent. crude anthracene cake from ordinary creosote oil, sold for pickling; even in the light oil, traces of anthracene were found.

* English patent, Jan. 24, 1874.

† Chem. News, xxxiii. pp. 99, 168.

‡ Private communication.

H. Günther * employs the filtered oil for manufacturing black printers' ink. It is to be boiled with 10 per. cent. of cupric chloride, which imparts a blackish-brown colour to it. The varnish is composed of 40 parts pitch or asphalt, 28 rectified oil of turpentine, 2 aniline violet, and $2\frac{1}{2}$ coal-tar oil.

Before anthracene, purified by any plan, can be converted into anthraquinone, it must undergo a suitable preparation (not merely by grinding) to reduce it to a sufficiently fine powder to facilitate the action of the oxidizing agents. For this purpose it is usually *sublimed* and precipitated in an extremely fine state of division by

Fig. 28.

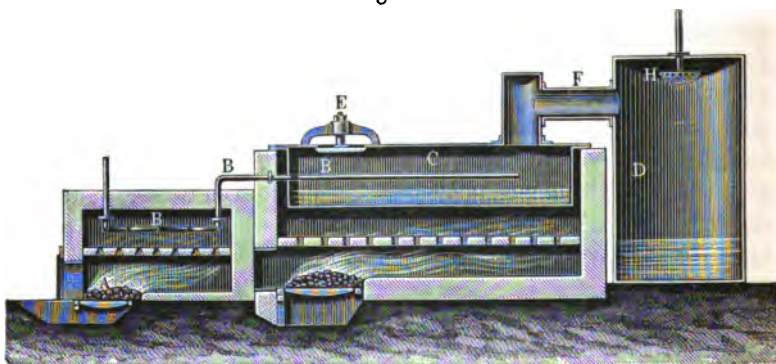
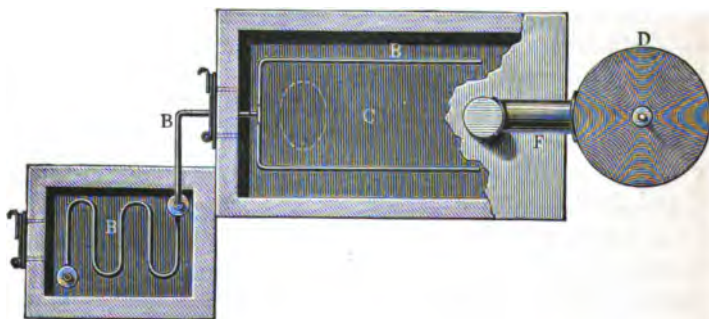


Fig. 29.



means of water. The sublimation is always effected by superheated steam, in an apparatus represented by figs. 28 and 29 †. The an-

* German Patents No. 9566 (Oct. 28, 1879) and No. 11930 (May 8, 1880).

† From Wurtz, Dictionnaire de Chemie, supplément, p. 95.

thracene is placed in a shallow pan C, made of boiler-plate and heated from below, so that the anthracene fuses and forms a layer an inch or two in depth. The steam arriving in the pipe B, is heated by the flame of the fireplace A to 220–240°, and issues from the flattened tube B' (which is perforated by many holes) to the melted anthracene, which it causes to sublime and carries away through the wide delivery-tube F into the brickwork or wooden chamber D. In this a jet of water, finely divided by the rose H, descends, condenses the steam, and suddenly precipitates the anthracene brought over in a state of finest division. The partial vacuum caused in this operation no doubt assists the sublimation in C. After draining, the anthracene, now a white mass of fine scales, can, after passing it through a sieve to separate any coarser particles carried along in the melted state, be oxidized while still wet. The loss in this operation amounts to two or three per cent. According to Wurtz the strength of the anthracene is thereby raised from 50 to 62–65 per cent.; according to Auerbach (*l. c.* p. 11) the effect of the sublimation is not a purification at all, but only a mechanical division. Probably the former takes place as well in the case of poorer qualities.

E. Perret (Wurtz, *loc. cit.*) proposes heating the anthracene to 250° and driving the vapour, mixed with air or carbon dioxide, by means of a fan-blast into chambers to be condensed in the dry way. A similar proposal was made by Schuller*; it does not seem so rational as the wet condensation.

The principal consumption of anthracene takes place in the German alizarine-works, which, according to reliable statistics, in 1880 worked up 1400 tons of *pure* anthracene, 200 tons of which were supplied by German tar-distillers, the remainder principally by English distillers.

The fluctuations in the price of anthracene are enormous. Perkin (*loc. cit.*) paid per lb. in 1870–71 1*s.* 6*d.*, in 1872 1*s.* 6*d.* to 5*s.* and even 5*s.* 6*d.* The present value is about 3*s.*

Properties and Analysis of Anthracene.

Rough anthracene, before sublimation, is a brownish-green friable mass, still containing most of the substances mentioned on p. 164. Looking at the high value of anthracene, and the extremely varying

* Ber. deutsch. chem. Ges. 1870, p. 548.

percentage of pure anthracene in the rough product, it is evidently of the greatest importance to possess a reliable method of analysis. Formerly this was merely attempted by the action of solvents for the impurities, which, however, is so imperfect that those methods have been almost entirely replaced by Luck's method, which certainly requires some manipulative skill. But as the old methods are not altogether obsolete yet, we must briefly describe them.

Each of them was intended to remove the foreign matters and to leave pure anthracene behind. Evidently this cannot be done with any approach to exactness; for, on the one hand, the impurities are not entirely soluble (some are even less so than anthracene itself) in the liquids employed; on the other hand, the latter dissolve sensible quantities of anthracene as well. Hence different solvents yield quite discordant results; but, apart from the evident impossibility of thus ascertaining the true percentage of pure anthracene, each method by itself gives pretty constant results, on the condition of strictly keeping to the same mode of manipulation, which must be agreed upon between buyer and seller. In the sale-note the solvent employed must be specified (*e. g.* whether carbon bisulphide or alcohol), its quantity, its specific gravity in the case of alcohol, and the exact way of manipulating it stated. Thus, if the product be of an oily nature, a higher value will be found if the sample be pressed before analyzing it, because the oils left in augment the solvent power of the liquid employed for anthracene itself.

The following are the methods employed in practice:—

1. *Alcohol Test (Spirit Test).*—Triturate the sample well in a mortar; weigh out 20 grams, which stir well up in a beaker with 150 grams of alcohol of the strength stipulated in the sale-note (usually sp. gr. 0.825); cover the beaker with a watch-glass, gradually heat to boiling, and then cool by placing it in water of 15°5. After an hour the liquid is decanted through a filter, and the undissolved part is gradually washed with alcohol of the same strength as before, and at the temperature of 15°5, till the filtrate and washings together amount to 400 cub. centim. If there is sand clearly perceptible at the bottom of the beaker, it is kept back; the remainder is placed in a weighing-glass, dried at 100° in a water-bath, and weighed. Its weight multiplied by 5 is accepted as the percentage of anthracene.

According to Auerbach (*loc. cit.*) 20 grams of anthracene cake

are heated with 100 cub. centim. of alcohol of 98 per cent., and the washing continued to a bulk of 300 cub. centim.

In order to test the so-called pure anthracene of this operation for foreign insoluble bodies, sometimes 5 grams are boiled with as much alcohol as suffices to dissolve all the anthracene, and the liquid is filtered while hot. The residue is washed with boiling alcohol; and the residue insoluble in this liquid is deducted from the percentage found above; if its weight amounts to more than 1 per cent., it must be considered an adulteration.

In any case the melting-point of the so-called anthracene is determined. It is put into a finely drawn-out glass tube, in which it is to occupy a space of about an inch in length; the tube is fastened by means of a small piece of elastic tubing to a good thermometer; and both are immersed in a paraffin bath, which is slowly heated. The point at which the first drop runs down is taken as the melting-point. After the mass has completely liquefied, the lamp is removed and the temperature at which solidification again takes place is observed. The mean between this and the point found above is the *mean melting-point*; it ought not to be below 190°.

Sometimes the following course is taken:—190° (or some other temperature) is accepted as the standard melting-point; and it is ascertained how much substance having this melting-point is obtained by employing an indefinite quantity of alcohol, but always of the same specific gravity (say 0.825). A sample is treated as above, and the melting-point ascertained. If this be 190°, nothing further is requisite; but if above that, a new test is made with less alcohol; if below, with more alcohol. If, say, sample No. 1 has been boiled with 150 cub. centim. alcohol and washed to 400 cub. centim., and has then yielded 40 per cent. melting at 195°, sample No. 2 is boiled with only 100 cub. centim. alcohol and washed to 300 cub. centim.; this yields more, say 49 per cent., melting at 188°. The quantity melting at 190° is then found by the proportion:—

$$195 - 188 : 49 - 40 = 195 - 190 : x,$$

where x is the amount to be added to the lower percentage. On carrying out the calculation we get

$$x = \frac{9 \times 5}{7} = 6.4;$$

hence the sample contains $40 + 6.4 = 46.4$ substance melting at 190° .

The spirit test is wrong in principle ; for alcohol dissolves some anthracene and does not remove the chrysene. These two opposite errors may compensate each other by accident, but certainly not in most cases ; and this method is therefore undoubtedly an inaccurate one.

2. *Bisulphide-of-Carbon Test*.—10 grams of the well-mixed sample are shaken in a stoppered bottle with 30 cub. centim. of carbon bisulphide, and allowed to stand an hour at $15^{\circ}5$. The undissolved matter is thrown on a filter ; the bottle is washed out with 30 cub. centim. of carbon bisulphide ; but any sand is left behind. After the liquid has run through, the filter is pressed gently, but quickly, first with the fingers and then between blotting-paper in a strong press. The insoluble matter is put on a watch-glass, dried for an hour at 100° , and weighed ; its weight, multiplied by 10, indicates the percentage. The "mean" melting-point of the substance ought not to exceed $212-214^{\circ}$.

Déhaynin heats 20 grams of anthracene with 40 cub. centim. of carbon bisulphide for 20 minutes, with constant stirring, cools down to 15° , filters through a tared filter, and washes with so much carbon bisulphide that the total amounts to 100 cub. centim. The residue is dried, weighed, and taken as pure anthracene.

Perkin grinds up 50 grams of anthracene with 10 fluid-ounces of petroleum spirit of sp. gr. 0.740, passes through canvas, and washes the vessel and the residue with another 20 fluid-ounces. The filter is squeezed out, first by hand, then in a vice. The residue is powdered, put into a bottle holding 6 or 7 ounces, and strongly shaken up for 2 or 3 minutes with 5 ounces of carbon bisulphide. It is then put upon a tared filter, pressed between blotting-paper, dried, and weighed. The product ought to show a mean melting-point of not below 200° , nor above 212° .

The bisulphide-of-carbon test, or the same combined with the application of petroleum spirit, has kept in use for a long time, although it is perhaps even worse than the spirit test. Chrysene is very little soluble in carbon bisulphide ; hence by this process a product may be obtained which shows the proper melting-point and yet is not anthracene. Besides, carbon bisulphide dissolves 2 per cent. of anthracene ; and, owing to its quick evaporation, very discordant results will be obtained by different chemists, according

to the difference of manipulation, the deviations extending to 4 or even to 6 per cent. ; 2 or 3 per cent. is quite usual here, as well as with the spirit test.

A comparison between the results of the spirit and bisulphide-of-carbon tests shows that the two do not bear a constant proportion to each other. In the case of low products the alcohol test indicates four times as much as the carbon-bisulphide test ; with higher percentages the discrepancy becomes less and less, the alcohol test uniformly giving a much higher result ; only at the highest percentages does the inverse ratio take place. There are also considerable differences between the melting-points. This is proved by a table given by Versmann as the result of 30 duplicate tests according to both methods.

ALCOHOL TEST.		CARBON-BISULPHIDE TEST.	
Percentage.	Melting-point.	Percentage.	Melting-point.
20	154	5	212
20	184	5	204
22	165	5	218
25	177	13	209
27	187	18	207
27	183	15	208
28	181	13	209
30	184	10	208
32	184	21	205
35	183	21	209
36	181	18	202
38	180	22	203
41	184	27	208
42	188	28	211
43	191	31	204
44	189	32	207
46	192	31	209
47	188	32	207
50	192	36	207
51	198	42	212
53	194	36	209
54	157	40	204
56	185	40	201
57	189	43	205
58	183	41	201
59	190	42	203
61	198	50	211
64	200	61	208
69	201	64	208
72.5	211	74	213

3. *Anthraquinone Test.*—It had been previously recognized that

the oxidation of crude anthracene to anthraquinone, and the estimation of the latter, is the only reliable method of analysis in this case. But the merit of investigating all the points necessary to elaborate a system of testing belongs to E. Luck, whose name is justly attached to this test. Luck had first to ascertain whether a weighed quantity of rough anthracene, on oxidation with glacial acetic acid and chromic acid, yields the theoretic quantity of anthraquinone, whether the latter is not oxidized further by long contact with chromic acid, and what is the behaviour of the regular (accidental or purposely added) accompaniments of anthracene during the chromic-acid treatment. Luck's results were as follows :—

I. Pure anthracene, dissolved in glacial acetic acid and treated at boiling-heat with 3–4 parts of chromic acid, yields 99·4 per cent. of the theoretically calculated quantity of anthraquinone.

II. Pure anthraquinone, dissolved as above and boiled with 3–4 parts of chromic acid for 2 hours, on dilution with water yielded the original quantity of the anthraquinone employed (employed 0·447, recovered 0·446 gram).—But more recent experiments refute this statement; by successive treatment of anthraquinone with constantly renewed quantities of glacial acetic acid and chromic acid 1 gram of 93·2-per-cent. anthraquinone was reduced to 0·576 gram. Hence anthraquinone does not resist the oxidizing action of chromic acid to the extent assumed by Luck.

III. The substances accompanying or contaminating anthraquinone are, by a sufficiently prolonged chromic-acid treatment, completely converted into bodies soluble in acids or alkalies, and can thus be separated from it. This holds good of phenanthrene, chrysene, paraffin, bitumene, &c.

Luck's method in its original shape was as follows :—

1 gram of the rough anthracene is dissolved in a small flask in 45 cub. centim. of boiling glacial acetic acid. If required, the solution is filtered quite hot through a small filter, and a solution of 10 grams chromic acid in 5 cub. centim. of water and 5 cub. centim. of glacial acetic acid is added in small quantities, so that the liquid remains constantly boiling. The chromic-acid solution is run in till a distinct and remaining greenish-yellow colour appears, or till after prolonged boiling a drop of the solution, put on a bright silver coin, produces after a few minutes a reddish spot of silver chromate. The liquid is now allowed to cool, is gradually

diluted with 150 cub. centim. of water, filtered after a few hours; the anthraquinone remaining on the filter is washed, first with water, then with hot very dilute solution of caustic potash, then again with water, and dried at 100°. After weighing, the anthraquinone is quickly removed from the filter, the latter is weighed, and its weight is deducted from the original gross weight. To the net weight thus obtained an addition of 0.01 gram is made, because, if according to the above prescription 50 cub. centim. of glacial acetic acid and 150 cub. centim. of water have been employed, 10 milligrams remained dissolved in the filtrate.—Commercial chromic acid often contains lead; in this case the anthraquinone, after washing with water and alkali, must be treated with a hot solution of ammonium acetate.

It was soon found that even in this way no perfectly accurate results were obtained. A portion of the impurities is not completely oxidized, and is thus estimated as anthraquinone. Hence Luck subsequently prescribed treating the latter with an alkaline solution of potassium permanganate. The anthraquinone, after washing with alkali, is washed into a small beaker or dish, is rendered faintly alkaline, heated to boiling, and a solution of potassium permanganate is gradually added, till it is no more reduced and the green colour is changed into pale pink. Now a little oxalic acid and sulphuric acid are added, to reduce the excess of potassium permanganate, and to dissolve the manganese dioxide formed. The whole is now filtered. Upon the same filter the precipitate is washed to perfect neutrality, then with dilute solution of sodium carbonate, then again with water, dried at 100°, and weighed. Luck states that usually 10 grams of chromic acid are quite sufficient, but exceptionally 15 grams may be required for perfect oxidation. Auerbach (*loc. cit.*) states that this indefiniteness sometimes produces awkward results. Thus a sample of rough anthracene, in four tests with 10 grams of chromic acid, always yielded 26 per cent., but in six tests, with 15 grams of chromic acid, only 23 per cent., although in both cases an excess of chromic acid was present. Probably a small excess of chromic acid in the presence of chromium acetate does not oxidize anthracene any further; this requires a larger excess. It would therefore be best to prescribe in all anthracene-contracts 15 grams of chromic acid for 1 gram of rough anthracene, which seems to be sufficient in every case. The time allowed for the oxidation has no influence:

three or four hours suffice ; and six or eight hours do not alter the result.

An objection to Luck's method is the hot filtration which is prescribed as sometimes necessary. Organic bodies are anyhow destroyed during the oxidation ; inorganic ones, which are mostly non-volatile, as sand, are best estimated by igniting a sample of crude anthracene. But if the substances insoluble in glacial acetic acid are to be estimated, it is in any case much safer to extract a weighed sample of crude anthracene completely, than to filter the mixture intended for analysis whilst hot, in which operation a portion of the anthracene is lost by evaporation of the acetic acid and crystallization on the filter.

J. T. Brown* proposes making the analyses more correct by taking a larger average sample, and by other precautions. He weighs off 50 grams of crude anthracene, and at the same time measures off 250 cub. centim. of petroleum spirit. With a portion of the latter he triturates the anthracene in a mortar so as to form a thin cream, pours it into a weighed filter (taking care to leave in the mortar any grit or sand that may be present), and employs the rest of the petroleum spirit in rinsing out the mortar and washing the precipitate on the filter. After draining, fold carefully, press between blotting-paper, dry at from 60° to 80°, and weigh. Crush the contents of the filter to fine powder, and weigh out the gram required for the anthraquinone test.—This proposal is useless ; for the temperature, the specific gravity of the petroleum spirit, &c. will essentially influence the result.

It is a further objection to Luck's method that even after treating with permanganate the anthraquinone is not yet pure. In this case it would dissolve without change in sulphuric acid, and would only at a temperature above 200° be converted into a sulphonic acid. But Luck's quinone when treated with concentrated sulphuric acid turns blue or brown, which proves the presence of foreign bodies ; even if the acid remains colourless, a coloured solution is obtained by subsequently boiling the quinone with dilute solution of caustic soda. Hence the results of purifying by permanganate vary from those of the purification with sulphuric acid (to be described anon) to the extent of from 1 to 8 per cent.

* Chem. News, xxxiv. p. 136.

For this reason Meister, Lucius, and Brüning* have proposed the following method of analysis, which is now well-nigh universally adopted. Take 1 gram of anthracene, put it into a flask with condenser of 500 c. c. capacity, add to it 45 c. c. of glacial acetic acid, and heat to ebullition. To this solution, which is kept boiling, add drop by drop a solution of 15 grams of chromic acid in 10 c. c. of glacial acetic acid and 10 c. c. of water. The addition of the chromic solution should occupy two hours, after which the liquid is kept boiling for two hours longer. The flask with its contents is to stand twelve hours, then to be mixed with 400 c. c. of cold water, and again kept standing for another three hours. The precipitated anthraquinone is now collected on a filter and washed, first with pure water, then with boiling dilute alkaline solution, and finally with pure water hot. The quinone is now washed from the filter into a dish and dried at 100° C.; it is then mixed in the same dish with ten times its weight of fuming sulphuric acid of 68° Baumé (sp. gr. 1·88) and heated to 100° C. for ten minutes on a water-bath. The quinone solution thus obtained is poured into a flat dish and kept for 12 hours in a damp place to absorb water; then add 200 c. c. of cold water to the contents of the dish, collect the precipitated quinone on a filter, and wash first with pure water, then with boiling alkaline solution, and finally with pure water hot. The anthraquinone is now placed in a dish, dried at 100°, and weighed. After volatilizing the quinone by heating the dish, it is weighed with the particles of coal and the ash. The difference between the two weights gives the weight of the anthraquinone obtained; and it is to be calculated in the usual manner into anthracene (multiplication by coefficient 0·8558). A correction for the quinone dissolved in the acetic acid is, under the conditions here prescribed, not necessary or admissible.

The following table (p. 186) will save a calculation.

According to the investigations of F. H. Davis and Lucast, the result of Luck's test does not at all agree with that of the carbon-bisulphide test; the latter mostly shows a great deal too much. But in one case Davis obtained from the same sample by the alcohol test (sp. gr. 0·825) 34·645 per cent., melting-point 187°·5;

* Zeitschr. für analyt. Chemie, xvi. p. 61.

† Chem. News. xxix. p. 169, xxx. p. 180, xxxi. p. 209.

Qui- none.	Anthracene.	Qui- none.	Anthracene.	Qui- none.	Anthracene.	Qui- none.	Anthracene.
1	0·86	26	22·26	51	43·65	76	65·05
2	1·71	27	23·11	52	44·50	77	65·90
3	2·56	28	23·96	53	45·35	78	66·77
4	3·42	29	24·83	54	46·21	79	67·62
5	4·28	30	25·67	55	47·07	80	68·46
6	5·14	31	26·53	56	47·93	81	69·32
7	5·99	32	27·38	57	48·78	82	70·17
8	6·86	33	28·23	58	49·65	83	71·02
9	7·71	34	29·09	59	50·50	84	71·88
10	8·56	35	29·95	60	51·35	85	72·74
11	9·42	36	30·81	61	52·21	86	73·60
12	10·27	37	31·66	62	53·06	87	74·45
13	11·16	38	32·53	63	53·91	88	75·32
14	11·98	39	33·38	64	54·77	89	76·17
15	12·84	40	34·23	65	55·63	90	77·02
16	13·70	41	35·09	66	56·49	91	77·88
17	14·55	42	35·94	67	57·34	92	78·73
18	15·42	43	36·79	68	58·21	93	79·58
19	16·27	44	37·65	69	59·06	94	80·44
20	17·12	45	38·51	70	59·91	95	81·30
21	17·98	46	39·37	71	60·77	96	82·16
22	18·83	47	40·22	72	61·62	97	83·01
23	19·68	48	41·09	73	62·47	98	83·87
24	20·54	49	41·94	74	63·33	99	84·73
25	21·40	50	42·79	75	64·19	100	85·58

by carbon bisulphide, 23·250, melting-point $198^{\circ}2$; by Luck's test, 28·358. Lucas found by the carbon-bisulphide test in three cases 0·4–2·7 per cent. too little, in seventeen cases 2·5–23·78 per cent. too much. He confirmed Luck's opinion that all the substances accompanying anthracene are by the chromic-acid treatment converted into bodies soluble in dilute alkali.

G. Schultz* points out that in one respect Luck's test gives too unfavourable a result, since chromic acid converts methylantracene into soluble anthraquinone-carbonic acid and thus removes it, whilst in actual manufacturing methylantracene is converted into a quinone, and this into methylalizarine, which has as much tinctorial power as alizarine. Methylalizarine, however, has not yet been shown to exist in commercial alizarine.

Holland† objects to Meister, Lucius, and Brüning's prescription (the "Höchst test") :—1st, the 55 c. c. of glacial acetic acid, diluted though it be with 400 c. c. of water, still retains anthraquinone in solution, viz. on an average 0·0023 gram; 2nd, that

* Ber. deutsch. chem. Ges. 1877, p. 1051.

† Printed circular, dated Manchester, Feb. 1879.

boiling water dissolves some quinone, viz. 500 c. c. water, 0.0019 quinone; 3rd, that in thrice washing the quinone from the filter a small loss is inevitable, which he estimates at 0.0020 gram; even with the most careful manipulation the total loss amounts to 0.0065 quinone = 0.0055 anthracene; and this quantity ought always to be added to that found. (According to information received by the author from the most competent quarter, Holland's corrections are inadmissible, as the anthraquinone obtained by the "Höchst test" is itself not quite pure, but contains methylanthraquinone, anthraquinone-carbonic acid, and paraffin, which may cause an error of 1 per cent. and upwards in the opposite direction to Holland's corrections.)

Schwarz* believes the best tests for crude anthracene to consist in washing it with a cold saturated solution of anthracene in glacial acetic acid. This test is not in use anywhere.

Lastly we shall mention a plan for *estimating the quantity of anthracene in tar*, although it does not appear to be very correct. C. Nicol† distils 20 grams of tar, and collects the vapours in a U-tube kept at 200° C. by means of a paraffin bath. Here the more volatile oils go away, whilst anthracene &c. remain behind. Since a little remains in the neck of the retort, this is cut off, the glass is pounded and added to the distillate in the receiver. This is now dissolved in glacial acetic acid, and the anthracene estimated by Luck's test.

* Wagner's Jahresb. 1877, p. 921.

† Zeitsch. f. analyt. Chemie, 1876, p. 318.

CHAPTER VII.

CREOSOTE OIL.

IN this Chapter we treat of the employment or further refining of those distillates from coal-tar which are midway between carbolic oil and anthracene oil. These are, in the first place, the fraction of coal-tar distilling directly between 240° and 270° , and, besides, from either side, the residues from the manufacture of carbolic acid, naphthalene, and anthracene. Practically every thing which cannot be used for any other purpose is run into the creosote-oil well. Since there are often very large stocks of this oil accumulating at the works, there must be correspondingly large store-tanks or wells, which need not be covered over, as the oil is not very volatile and the rainwater floats on the top of it, whilst the pumps take it away from the bottom. Still it is safer, as a precaution against fire, to cover up the tanks. At La Villette the creosote oil is kept in large upright cylindrical tanks, standing on brick pillars over a water-tank visible and accessible from all sides. Thus any leakages are noticed at once, and in any case the oil is prevented from penetrating into the ground. Where this is of no great consequence, the oil-tanks are mostly partially or entirely sunk in the ground. They are better if made of boiler-plate, than of brickwork set in cement.

According to Watson Smith it is advisable to fix a steam-pipe, so that the naphthalene crystallizing out can be dissolved again before any large quantity is sent out.

Creosote oil (heavy oil, dead oil), when fresh, is light greenish-

yellow and strongly fluorescent, being rendered still more fluorescent by the action of air and light. After some time it turns much darker and is bottle-green by reflected, dark red by transmitted light. As the distillation proceeds, it becomes darker and darker, and more consistent. Its smell is extremely characteristic—unpleasant, almost nauseous. It is as thick as oil, and at first has also an oily touch, but soon acts upon the skin by its acids. It is always heavier than water; the specific gravity of its last portions is 1.070.

The following bodies have been found in creosote oil:—naphthalene, methylnaphthalene, anthracene, phenanthrene, and the hydrocarbons coming in between these; phenol, cresol, &c.; aniline and all the other bases mentioned in Chapter II. (p. 69 *et seq.*); lastly, probably as the principal constituent, so-called “indifferent” oils, liquid at the ordinary temperature. Of these, in spite of the enormous quantity constantly produced, hardly any thing is known. Up to this moment the separation and purification of the several oils belongs to the unsolved problems of chemistry. Only one of these liquid oils, β methylnaphthalene, has as yet been isolated (p. 48).

We get an important insight into the nature of creosote oil (as well as anthracene oil) by the following results, obtained by Watson Smith with the distillation from Lancashire tar. Sample No. 1 was taken after 150 gallons had come over; No. 2 was a sample of the next 100 gallons; No. 3, of the next 100 gallons; No. 4, of the first “red oils;” No. 5, of the last oils.

No. 1 was of light colour, and on cooling was almost entirely solidified by the crystallization of naphthalene.

No. 2. Yellowish oil, with few crystals of naphthalene.

No. 3. Quite similar.

No. 4. Red oil, with but little deposit.

No. 5. Red oil, solidifying on cooling.

All contained a little water. All of these samples were distilled, with the following results in percentages by volume (N signifies that, on cooling, naphthalene began to crystallize; O, that all remained liquid; A, that anthracene began to crystallize):—

Temperature.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	per cent.	per cent.	per cent.	per cent.	per cent.
Up to 180°	1.0	6.6	1.0	2.7 O
" 210	6.3 N	4.7 N	2.0	1.1
" 220	10.0	16.0 N	1.6	8.3 N	0.7
" 230	12.0	5.5	7.6	2.0	0.7
" 240	14.3	13.8	1.8	4.7	0.9
" 250	13.3	9.8	8.3 O	3.3
" 255
" 260	9.3	4.9 O	9.3	9.7	0.7
" 270	7.0 O	8.9	1.6 O	12.0 A	1.8
" 280	4.3 A	4.9 A	8.7	8.7	1.8 A
" 290	3.7	3.5	6.6 A	5.4	1.8
" 300	3.7	3.8	11.3	4.3	5.9
" 310	3.7	2.1	4.5	3.0	12.0
" 320	3.7	2.8	1.3	7.3 {	8.2
" 330		4.0
" 335	6.0 {
" 340	2.8
" 345
" 350	2.1	18.0 {
" 360	1.6	
Above 360.
Yellow crude anthracene	7.1	4.8	18.0	34.0
Orange or red substance.	1.8	4.3	5.3	16.0
	99.4	87.5	97.8	97.7	95.6
State of the pitch remaining behind on rectification	good.	very good.	half cooked.	hard.	{ beginning to coke.
<i>Totals.</i>					
Crystallizing naphthalene oils	66.2	45.1	33.3	15.0	0
Not crystallizable oils	7.0	13.8	10.3	9.7	11.9
Anthracene oils	26.2	28.6	47.6	70.0	83.7

Heavy coal-tar oil has hitherto been put to the following uses :—

- 1st. Rectification, to obtain more valuable products.
- 2nd. Passing through red-hot tubes, to obtain illuminating-gas and more readily saleable hydrocarbons.
- 3rd. Pickling timber.
- 4th. Softening hard pitch.
- 5th. Preparation of varnishes.
- 6th. Lubricating-oil, either in the crude state or after some preparation ; also for preparing cheap mineral paints, in lieu of linseed-oil.
- 7th. Burning for heating-purposes.
- 8th. Burning for lampblack.

9th. Lighting.

10th. Carburetting gas.

11th. As an antiseptic.

Of these uses, the *softening of hard pitch* and the *preparation of varnishes* have been treated in pp. 149 and 152. Neither need we here dwell upon the *burning for lampblack*, which in some places consumes a large portion of the heavy oil, since this is done exactly in the same way as described on p. 81 for tar itself. We shall therefore only describe the other uses of creosote oil.

Rectification of Heavy Oil.

This operation is only carried on in a few localities, *e.g.* in Scotland. Its object is, getting out as much as possible of the more valuable constituents. The oil is distilled in ordinary tar-stills; and the same kind of fractions are obtained: the result is a very small quantity of light oil, then a little carbolic oil, again the bulk of heavy oil, and at the close some pasty anthracene oils, which are added to those obtained in the direct distillation of the tar. The middle fraction, which preponderates, is used up in the manner previously detailed. No doubt this is the most rational way of working up the heavy oils; but the expense of fuel, wear and tear, wages, and the unavoidable loss seem to deter most distillers from following it. Probably distillation in a vacuum would be the best plan.

Even more rarely will it pay to wash the heavy oils with sulphuric acid and caustic liquor before distilling them. The former takes up the basic bodies, but along with them a large quantity of other compounds (in the shape of sulphonic acids); the bases themselves are extremely difficult to separate (p. 73), and are employed for no technical purpose—except aniline, which is made much more cheaply from benzene than from heavy oil, the latter containing it ready formed, it is true, but only in minute quantity. The caustic-soda liquor dissolves the phenols; but for preparing pure carbolic acid the carbolic oil proper is much better adapted; still it sometimes pays to extract the phenols from heavy oil by an alkaline treatment.

It is stated by some that the heavy oils, after washing with acid and alkali, can be freed from the nauseous smell by being shaken up with 4 per cent. of their weight of ferrous sulphate, which removes certain sulphur compounds.

In the distillation of heavy oil, washed in the above manner, the

first fraction (from 215° or 220°) will consist essentially of naphthalene, which, as well as the last fraction (containing anthracene), is collected by itself. The middle portion is adapted for lubricating-oil, for preparing paints, for illuminating-purposes (see below), &c. Wurtz* recommends the following treatment. The heavy oil is distilled in boilers holding 1000–2000 litres; and the following are collected:—1st, the products below 120°, which go to crude benzol; 2nd, the products between 121° and 190°; 3rd, the residue, which goes back to the tar. The second fraction [between 121° and 190°?] is washed with acid and alkali, and is then sold for lubricating, or for pickling timber, or else it is converted into an illuminating-oil. For this purpose the naphthalene should be removed by treating with 10 per cent. concentrated sulphuric acid, then with water, then with 6 per cent. concentrated solution of caustic soda. The oil is now rectified; and the distillate is agitated with ferrous sulphate (compare p. 191).

The oil thus purified is sold as “*huile sidérale*” †.

Decomposition of Heavy Oil by Heat.

For a long time past attempts have been made, partly successfully, to utilize otherwise comparatively valueless oily residues by exposing them to a high degree of heat, *e.g.* passing them through red-hot tubes. Usually the main object was that of making illuminating-gas; but with this was associated the getting of more valuable oils. We have seen in Chapter I. that both benzol and anthracene can be obtained in this way from the heavy residues of petroleum, browncoal-tar, and wood-tar. Many chemists have worked in this direction, mostly with browncoal- or peat-oils, as Breitenlohner‡, Vohl§ (who believes this process to be practicable), Walker and Smith||, and others. An apparatus specially con-

* *Matières colorantes*, p. 33; *Dictionn. de Chimie*, i. p. 651.

† The author has not been able to discover that any “*huile sidérale*,” made in the manner described by Wurtz or in any similar manner from coal-tar oils, is sold anywhere. It is possible that in this case again there has been some confusion with paraffin oils; but even if it be otherwise, we can only say that the above process must have been given up long since, as at the present prices of illuminating-oils it could not possibly be remunerative.

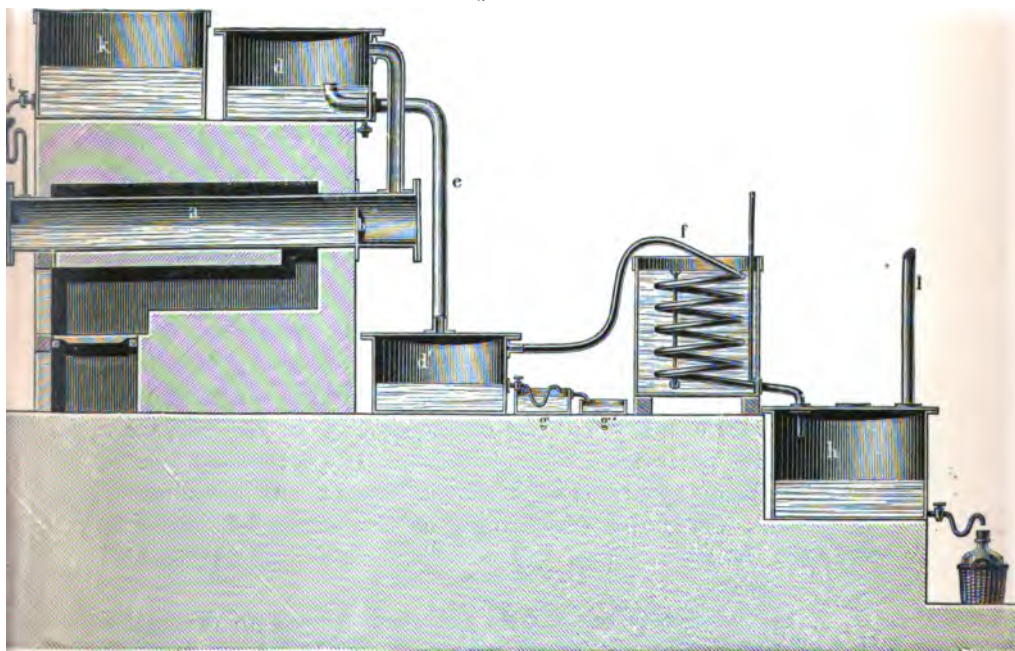
‡ *Dingler's Journal*, clxvii. p. 378, clxxv. p. 392.

§ *Ibid.* clxxvii. p. 58.

|| *Wagner's Jahresh.* 1867, p. 752.

structed for the case in question was patented in 1861 by the Paris Gas Company*; it is represented in fig. 30. It consists of a set of cast-iron cylindrical retorts *a*, closed at one end and provided at the other end with a movable cover. About 12 inches from one end there is a partition *b*, 8 or 12 inches high, which prevents the oil from running towards the part not exposed to the fire. The space thus shut off communicates by an ascending

Fig. 30.



pipe, *c*, with a receiver, *d*, which is connected by *e* with another receiver, *d'*, equally intended for heavy products of condensation : these are removed by the pipes *g g'* ; whilst the vapours not yet condensed pass through the worm *f* and are collected in *h*. *l* carries away the incondensable gases. The heavy oil runs from the tank *h* through a tap, *j*, into the funnel *i*, and thence in a continuous stream into the retort *a*, previously brought to a red heat. There the oil spreads as far as the partition *b*, and is

* *Technologiste*, 1861, p. 145 ; Girard and Delaire, *Dérivés de la houille*, p. 20.

decomposed into graphite (remaining in the retort) and volatile products (passing over the partition and through the pipes into the receivers). In *d* and *d'* a heavy, tarry liquid condenses; it is mixed with more heavy oil and again run back into the retort [nowadays it would probably first be worked for anthracene]. The liquid condensed by the worm *f*, and collected in *h*, is rich in benzol, and is treated like ordinary crude naphtha. The gas escaping at *l* is employed for lighting, and was at that time considered the principal product.

Behrens* employed for a similar purpose a retort made of fire-bricks, heated from below. It was heated up to a very bright red heat; and a continuous jet of heavy oil was run into it by a swan-neck pipe. The volatile products were condensed by an ordinary hydraulic main and by very wide pipes, which nevertheless were frequently choked up with naphthalene and soot. In the hydraulic main (at the base of the furnace) most of the undecomposed oil was condensed; the remainder, together with naphthalene and the more volatile hydrocarbons newly formed, condensed in the cooling-pipes. In this way the heavy oil yielded on an average 2 per cent. benzene and toluene, and a little xylene and higher homologues. Below and above the temperature above mentioned less of the more volatile hydrocarbons was formed. In the former case but little heavy oil was decomposed†; in the latter the benzene was converted into naphthalene. In the furthest part of the condensing-apparatus naphthalene, benzene, and toluene were collected. The graphite remaining on the furnace-bed could be obtained in large pieces, and was valuable for producing high temperatures.

At the present prices it does not seem to pay to decompose heavy oil in this way—except perhaps in the few cases where gas companies distil their own tar, and cannot get rid of the creosote oil, so that it is best to turn it into gas.

According to J. Young, heavy paraffin oils can be converted into light ones by heating them in strong iron boilers under a pressure of $1\frac{1}{2}$ atmosphere. Possibly this would apply also to heavy coal-tar oils; but evidently nothing can be said as to the probable cost, yield, and so forth.

* Dingler's Journal, ccviii. p. 361.

† Hence the cast-iron retorts patented by the Paris Gas Company cannot have stood a very long time, as they would have to be heated too high.

Employment of Heavy Oils as Lubricants.

This can be rationally done only after removing the phenols (acids), which promote friction. Naphthalene also will hardly be favourable to lubrication. But the mixture, hitherto very little known, of non-solidifying oils, which come before and along with anthracene, is really a lubricant, at least after proper treatment. Still it seems doubtful that coal-tar oils will be largely used in this way; the heavy paraffin and petroleum oils and rosin oil are far superior lubricants, and are nowadays cheap enough to make the employment of coal-tar oils superfluous.

In order to prepare the latter for this purpose, the phenols (commonly called "acids") must be removed. This would be done effectually by the treatment mentioned on p. 191; but as this is mostly too expensive, the cartgrease-manufacturers treat the oils with lime, similarly to rosin oils, with which they are generally mixed. Thenius * prescribes gradually adding to a hundredweight of crude rosin oil, contained in a retort, 56 lb. of slaked lime, and heating, with agitation, till the whole is dissolved, then distil for an hour, condensing the vapours. The mass is now allowed to settle; and the clear portion is run off. On the other hand, $1\frac{1}{2}$ cwt. of dry slaked lime is mixed in an open pan with $\frac{1}{2}$ cwt. of rosin-oil and $\frac{1}{2}$ cwt. of heavy coal-tar oil freed from acids; the mass is stirred and heated till it is quite homogeneous, and is then allowed to cool while being constantly agitated. Of each of the two mixtures thus prepared $\frac{1}{2}$ cwt. is taken; they are mixed up in a pan; and, with constant stirring, a third mixture is added, consisting of 23 lb. of melted ozokerite, $\frac{1}{2}$ cwt. of heavy coal-tar oil free from acids, and $\frac{1}{2}$ cwt. of heavy rosin oil. The latter mixture is added when it has cooled down to some extent, but before it has solidified. It may be coloured yellow with a few pounds of turmeric, or blackish blue by lampblack.

Thenius also describes another kind of cartgrease, made of a mixture of a tallow soap, fish-oil potash soap, and coal-tar oil.

Dumoulin and Coutelle prepare lubricating-oil by stirring up 2 cwt. of creosote oil, 11 gallons of water, 2 lb. of bleaching-powder, 2 lb. of soda ash, and 1 lb. of manganese, settling 24 hours, decanting the clear liquid, distilling it, and mixing the distillate with one fourth of its weight of rosin oil: this treatment is to

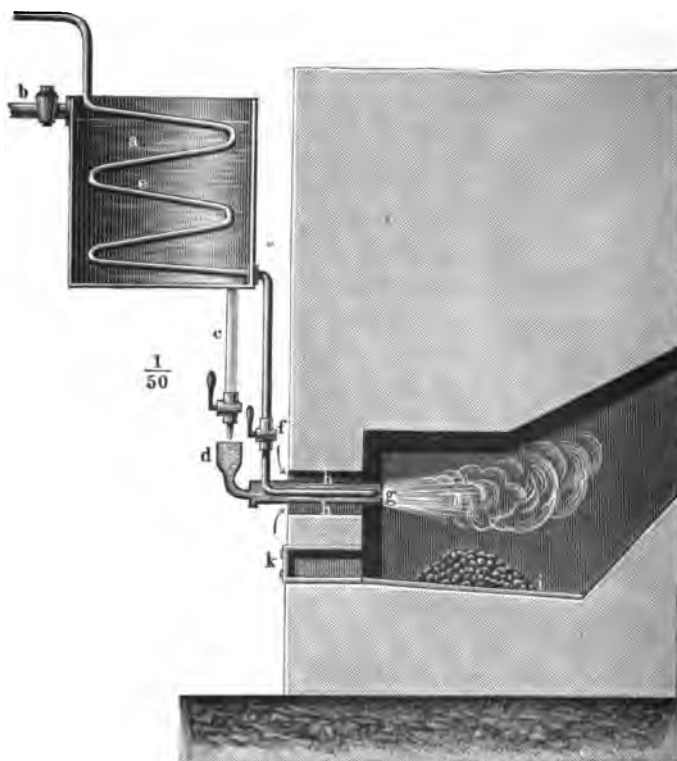
* Verwerthung des Steinkohlentheers, p. 82.

remove the "gummy" part of the tar-oils and to make them inodorous. Or else the oil may be distilled before adding the ingredients.

Burning Heavy Oils for Heating-purposes.

Where those oils cannot very well be utilized they are sometimes burnt—for instance, for heating the tar-stills themselves. Fig. 31

Fig. 31.



shows how this can be done. *a* is an iron tank for creosote oil, which runs in from a tap *b*, best constructed as an automatically acting ball-cock, so that the level shall remain always the same, and the oil run off in a uniform stream through the pipe and out of the tap *c*, in an open jet (so that any choking-up can be at once observed) into the funnel *d*, and from this into a horizontal iron

tube, *g*, which ends inside the fireplace. In the centre of the oil-pipe is a steam-pipe *f*, which first passes as a worm, *e*, through the oil-tank *a*, and keeps it always warm. A cock, *f*, permits the regulation of the steam jet, which, as it issues in the centre of the oil-tube's extremity, converts the oil into a fine spray, and at the same time, acting as an injector, carries in through the open space *h*, which surrounds the pipe *g*, the air necessary for combustion.

Fig. 32.

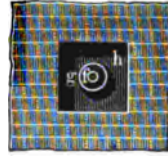
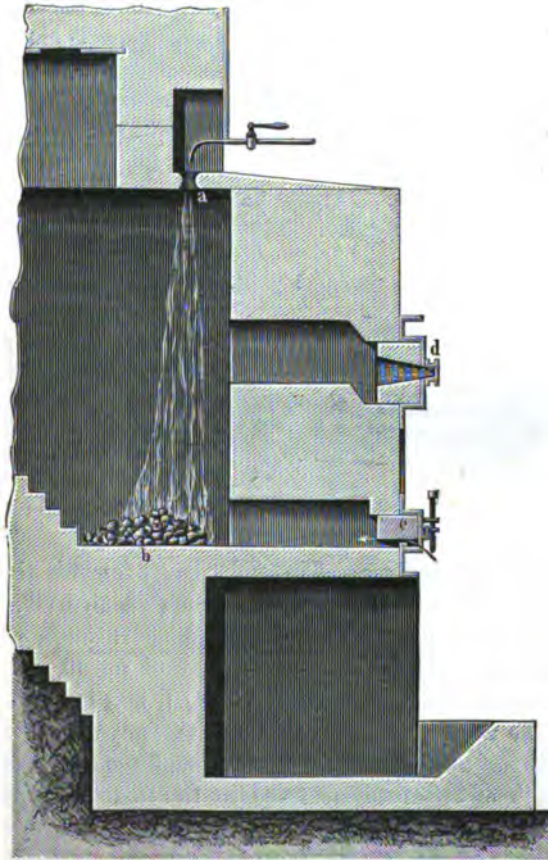
 $\frac{1}{50}$

Fig. 33.



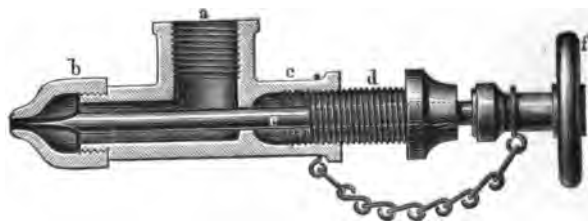
Thus the oil mist is brought into very intimate contact with air

and is almost instantaneously burned; a little of it falls down upon the plate *i*, where it burns into coke, which is removed from time to time through *k*.

Fig. 33 shows a contrivance for burning the oil without a steam jet, by Liegel *. It was originally intended for heating gas-retorts by tar. The tar drops through an opening, *a*, $1\frac{1}{2}$ inch wide, upon a plate, *b*, 5 feet 3 inches below, which reaches through the front wall and is shut off by the door *c*. The latter consists of a slide moving air-tight on its bed by means of a screw. The air for combustion enters below the slide, and first meets a bed of red-hot tar-coke, collecting on *b*, which it burns into light-grey ashes. The tar is partly burned by the radiated heat of the fireplace; but most of it falls onto the tar-coke burning below, is spread out, and meets the air coming in from the door-slide. The small door *c* is opened every half hour for loosening the coke and getting out the ashes. Another door, *d*, with a peep-hole, is placed higher up, and is likewise to be closed air-tight.

Schilling (ibidem, p. 324) also figures a special "squirting cock" for the tar, shown in fig. 34. The vertical branch *a* is screwed

Fig. 34.



upon the tar-supply pipe. The end turned towards the furnace is closed by a cap *b* with an opening about $\frac{1}{16}$ inch wide. The other horizontal end, *c*, is provided with a gland through which passes a long screw, *d*, which carries a horizontal needle, *e*. The outer end of *e* is provided with a small wheel, *f*, and is fixed by a small chain. The needle serves for partly or entirely closing the opening (that is, for regulating the jet of tar), also for cleaning it out in case of need. The apparatus is fixed in the furnace-front, so that a slide can be put in front of it.

In the case of gas-retorts there ought to be on the fireplace-bed

* From Schilling's 'Gasbeleuchtung,' 3rd ed. p. 325.

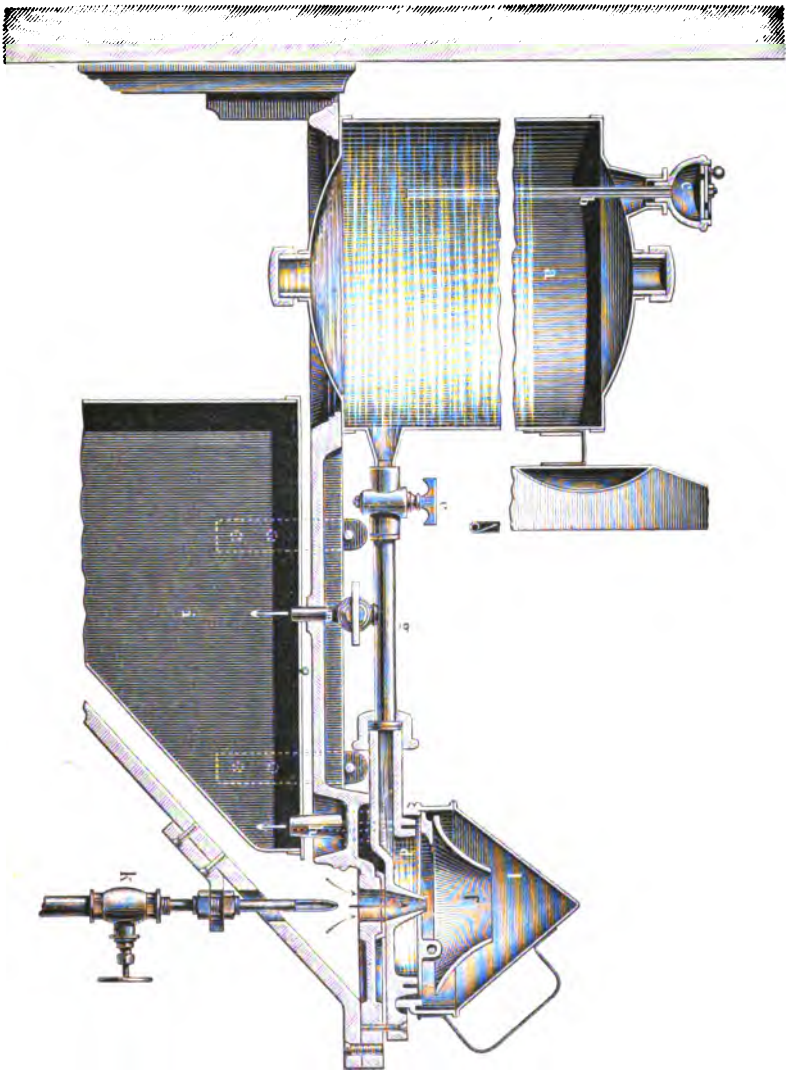


Fig. 35.

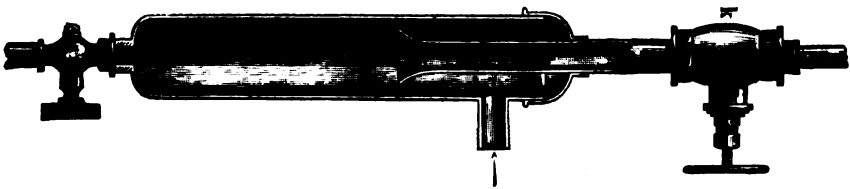


Fig. 30.

a 4-inch layer of hot coke which is broken up every half or three quarters of an hour. The bed ought always to be dry; otherwise too much tar has been run in, or too little air has been admitted. For the purpose of making a start, a small wood fire is made on the hearth, and the tar is run in at once. 100 parts of tar are about equivalent to 200 parts of coke.

Employment of Creosote Oil for Lighting.

This has long been done in the construction of harbours, railways, &c., where the smoke was of no consequence. But this burning in open pans is a most wasteful, crude sort of illumination. The process of Dumoulin and Coutelle (p. 195) was intended to make creosote oil fit for lighting even dwelling-rooms; but that degree of success is very doubtful. In order to get a proper lighting-effect, it is indispensable to introduce a jet of air, which prevents the formation of black smoke and burns the soot. Hence every thing depends upon the construction of the *lamps*. Probably the best lamp for this purpose is the steam-jet lamp of Hartmann and Lucke*, shown in figs. 35 and 36. The steam-jet serves not merely to convey the oxygen necessary for combustion, but also to decompose the carbon compounds, thus preventing the formation of soot and producing an intense light. This lamp can of course be employed for any cheap petroleum or tar-oils, but is specially intended for ordinary creosote oil; it does not require a mechanical blast, but can be placed wherever steam can be had, and is thus principally adapted for lighting large factory workshops, yards, &c., but not for places which require a less intense and more divided source of light.

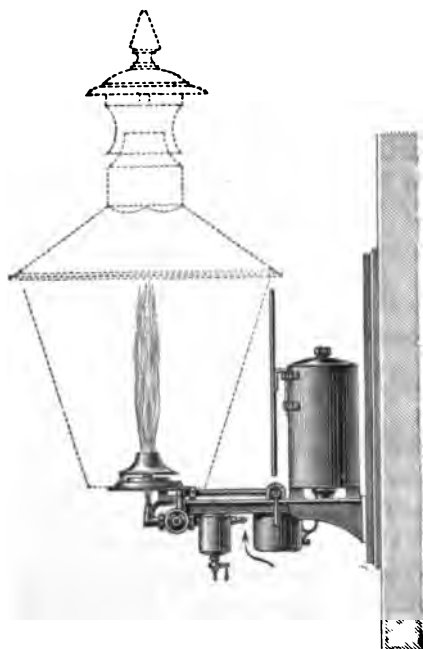
In the vessel *a*, filled with oil, is suspended the air-supply pipe *b*, ending at the top in a funnel, *c*, provided with a slide to regulate the supply of air to the vessel *a*. Hence the oil must flow out of *a* quite evenly, on Mariotte's principle, the pressure being constant. It flows through the cock *e* and the pipe *g* into the plate *d* (which must be mounted in a perfectly horizontal position), where it is lighted and then covered with the funnel *f*: as the oil is difficult to light, it is first covered with a little petroleum. Steam, first dried in the apparatus *k* (fig. 36), is now, very slowly, admitted through the conical opening in the plate *d*. As soon as the oil burns equally all over the plate, which is brought about by

* German patent, No. 9195, Aug. 9, 1879.

regulating the steam-supply, the lamp requires no more attention. If by a wrong position of the slide at *c* the plate is supplied with more oil than can be burnt, the superfluous part overflows into the annular channel round the plate and through the tube *h* into the vessel *i*. At first it is best to let it overflow; afterwards, when the oil has got hot, its supply is regulated so that the inner part of the plate always remains full. To put out the lamp the cock *e* is shut (so that no more oil flows into the plate), the steam is shut off by the cock *k*, and the flame is extinguished by putting on the funnel-shaped cover *l*. The oil remaining in *d* and *g* is run into *i* by opening the tap *m*. This is a threeway cock, which either conveys the oil to the burner, or else discharges it into the vessel *i*.

The steam admitted underneath the plate *d* acts mechanically

Fig. 37.



by forcing the air necessary for combustion into the flame, and also aspirating the air from without through the openings beneath the funnel *f*. The steam also acts chemically upon the hydro-

carbons, forming a gaseous mixture which on combustion produces an extremely brilliant light, and no soot. This is not attained by ordinary lamps, because in those, when enough air is admitted, the flame becomes hotter but not more luminous. The steam should be as dry as possible; and the condensed water must be allowed to run away.

Thus the tar-oil burns without wick or chimney, preferably in very large glass lamps with reflectors. Such a lamp gives a light of 20 ordinary gas lights or 180 standard candles, with an hourly consumption of about $2\frac{1}{2}$ lb. of tar-oil. The oil-vessel holds about 7 gallons, so as to suffice for the longest winter nights. The lamps need no cleaning or repairing.

The most recent form of this lamp is shown in Fig. 37, $\frac{1}{2}$ natural size; this shape costs £5 including package, the glass lamp £4. Where the carriage does not make the oil too dear, this light is much cheaper than gas-light.

The employment of creosote oil for *carburating gas* will be discussed later on, along with that of other tar-oils (Chap. X.).

As an *antiseptic*, creosote oil is but exceptionally used; for this purpose either crude tar or else its phenols by themselves are justly preferred. Dusart * asserts, however, that precisely the portion distilling between 210° and 300° , when freed from excess of naphthalene, acts energetically in preventing the further putrefaction, and destroying the smell, of faecal matters, even in fractions of 1 per cent.

Employment of Creosote Oil for Pickling Timber.

That wood can be protected for a long time from decay by painting with coal-tar or coal-tar oils, has been long known (p. 79). But the rise and progress of this industry, which nowadays consumes the larger portion of all the heavy coal-tar oils produced, began with Bethell's patent (1838), which treats of the impregnation of railway sleepers &c. under high pressure.

In Europe the plan universally pursued is that introduced by Bethell. The timber (previously dried) is put on iron bogie-frames, which are run upon rails into very strong horizontal wrought-iron cylinders, 6 or 7 feet in diameter, 30 feet long, $\frac{3}{8}$ inch thick. The front is then firmly closed by a cover. Now the air is

* Compt. Rend. lxxix. p. 229.

exhausted (this was first proposed by Bréant) ; and when this has been sufficiently effected, communication is opened by a cock with a tank holding the creosote oil, heated to a temperature of about 50°, at which it is perfectly fluid. The oil at once rushes into the vacuum and deeply penetrates into the pores of the wood, whilst otherwise the air contained in them would pertinaciously resist the entrance of the oil. When no more oil is sucked up, a force-pump is started, which presses more oil into the cylinder, till a pressure of 8 or 10 atmospheres has been attained. This is kept up for several hours ; and the wood in this operation absorbs on an average nearly a gallon per cubic foot.

In America, Pelton's apparatus* is much employed. Here the wood (which may be used in the green state) is covered with creosote oil in iron cylinders, heated for some time to 100° or 110°, so that the water evaporates ; and then fresh cold oil is run into the cylinder. The hot oil already contained there now penetrates into the pores of the wood, a partial vacuum being caused by the cooling. The apparatus is figured and described in detail in the place quoted. It is very doubtful whether in this way the impregnation will be as thorough as in the European process ; and the only essential advantage, that of avoiding the high pressure, will hardly make up for this.

Vohl† proposed to add to creosote oil enough caustic-soda liquor to make it miscible with water, painting the wood several times with this liquor, and ultimately fixing the creosote by a dilute solution of ferrous sulphate. This plan does not appear to have been practically tested.

The creosote treatment is also applied to sails, ship's ropes, fishers' nets, &c., and protects these better than the usual tarring. The objects are first "tanned" by treating them with a dilute solution of glue and then with a bath of tanner's bark. Thus glue is precipitated within the vegetable fibre, which is now enabled to fix the creosote oil in the subsequent treatment, and retain it even in sea-water.

The advantages of pickling wood with tar-oils, or "creosoting," are both chemical and mechanical. The principal chemical action of coal-tar creosote is ascribed to its "acids," *i. e.* the phenols,

* Ott, in Wagner's Jahresh. 1874, p. 959.

† Dingle's Journal, cxvii. p. 448.

which certainly coagulate the albumen and consequently render animal life impossible. This, along with the now universal assumption that putrefactive decay can only occur in the presence of microscopic organisms, whose vital process is an indispensable condition of it, would by itself explain why timber impregnated with phenol cannot decay, provided that the phenol is not removed again by washing &c. Hence the value of creosoting-oils would be parallel with their percentage of phenols. Others contradict this, and assert that the "indifferent oils" participate essentially in the preservative action of coal-tar creosote. In any case the last-mentioned oils play a principal part in the *mechanical* effects of creosote oil, which are no doubt very important. The oil, being forcibly drawn into the wood by a vacuum and then driven in by high pressure, closes up all pores and, as it were, agglutinates all the parts so that no water can penetrate, without which those organisms cannot develop and the wood cannot decay. This also prevents the phenols from being washed out by the subsoil water. Even larger insects and other vermin are kept away by the smell of creosoted wood. Some have asserted that even the *Teredo navalis* spares creosoted wood; but others deny this.

It has long been disputed what part is played by the *naphthalene* in creosote oil. We know that it occurs abundantly therein, and crystallizes out on the cooling of the first fraction of this oil. Its quantity is increased by the residue from working the light oils for benzols, phenols, &c., which is extremely rich in naphthalene, going to the creosote oil. This, as it arrives at the creosoting-works, is often quite pasty with naphthalene. In the pickling process the oil is heated to 50°, so that the naphthalene is dissolved; and only on the cooling of the pickled wood does it crystallize again, among the other constituents of the oil, the coagulated albumen, &c. It was formerly believed that this was injurious to the preservation of wood, perhaps by the naphthalene volatilizing and leaving empty spaces which might be filled with moisture and become breeding-places for putrefactive organisms. Hence, as we shall see, several creosoting-works have fixed a maximum for the naphthalene, which causes great inconvenience to the tar-distiller, since very much more naphthalene is produced than can as yet be consumed.

But it seems that the objection to naphthalene in creosoting is quite unfounded. In the first place, naphthalene itself is un-

doubtedly a disinfectant and prevents the development of lower organisms. Secondly, as has been proved by Dr. C. Meymott Tidy*, the total loss by evaporation of naphthalene is very small, and takes place almost exclusively during the first day or two after the wood has come out of the creosoting-apparatus. During the first and second day some naphthalene volatilizes from the surface of the timber; but after this there is no more loss of weight, and the interior of the wood is quite unchanged. According to Dr. Tidy the naphthalene is useful both chemically and physically; it cannot possibly do any harm; and the condition that creosote oil should be free from it, seems quite uncalled for.

The following different requirements are made by some English and foreign creosoting-works :—

Specification made by...	Dr. Letheby.	Great Western Railway Co.	Chemin de fer de l'Est (France).	Chemin de fer de l'Ouest (France).	Chemin de fer de l'Etat Belge.
Spec. grav....	1.045-1.055 at 60° F., but as nearly as possible 1.050.	1.045-1.055 at 60° F.	1.030 at 35° C.		
Deposit when cold.	Should not deposit any naphthalene at 40° F.	Should not deposit more than 30 per cent. at 40° F.	Not above 30 per cent. deposit (temperature not stated).
Yield of coal-tar acids.	5 per cent. crude carbolic acid and other coal-tar acids.	10 per cent. acids, of which 5 per cent. crude carbolic acid.	8 per cent. phenol.	5 per cent. phenol.	
Heat and quantity of distillate.	Should not yield less than 90 per cent. at 600° F.	Not less than 90 per cent. at 600° F.	One third should distil at 200°-250°, two thirds above 250° C.
Heat and liquidity.	Should be perfectly liquid at 35° C.		
Further requirements.	Should be of "first quality."	

* In an official (unpublished) report kindly placed at the author's disposal by Dr. Tidy.

Dr. Tidy comments upon the above table in substance as follows:—

1. The *specific gravity* cannot be taken with certainty at the ordinary temperature, because the substances suspended in the oil act in a disturbing manner; hence it is necessary to work at a temperature at which all is liquid. It should be noticed that nowadays anthracene is always worked for, which was not the case at Dr. Letheby's time; this necessitates a higher temperature in the tar-stills and a higher specific gravity of the distillates. It does not seem necessary to fix any point in this respect; eventually a maximum of 1.065 at 60° F. or 1.040 at 100° F. might be stipulated.

2. *Deposit of naphthalene*.—It seems quite unnecessary to stipulate for its absence; but it is indispensable that the oil should be quite fluid at the temperature at which the creosoting takes place. For this temperature 100° F. (=38° C.) can be taken; and it is ascertained in this wise: (a) the oil is heated with a thermometer immersed till all is clear; (b) it is heated till quite clear, then it is allowed to cool and the temperature at which it becomes turbid is observed. The latter observation is much safer than the former; and as the solidifying-point is about 10° F. below the melting-point, it is best to stipulate that no turbidity shall set in above 90° F. (=32° C.).

3. *Coal-tar acids*.—Their estimation is not a very simple matter. Under all circumstances it is necessary to work with caustic liquor of exactly the same concentration and with the greatest possible uniformity in all the other experimental conditions. A prescription of the percentage of real carbolic acid (C_6H_5O) is useless, as there are no reliable methods known for separating it from the other phenols. Hence only a certain quantity of all the tar-acids *in toto* should be required, for which a minimum of 9 per cent. may be assumed*. The plan recommended by Dr. Tidy for estimating the tar-acids is mentioned below, together with that recommended by Prof. Abel.

4. *Behaviour in distillation*.—This is examined in a glass retort which is quite submerged in an oil-bath, lest any distillate should condense on the sides of the retort. The highest temperature is 600° F. (=315° C.), at which 85 per cent. should have distilled.

* According to Dr. Tidy's latest communications, he has agreed with Prof. Abel upon 10 per cent. tar-acids, half of which should be phenol and cresol.

Tidy's Process for Estimating the Coal-tar Acids.

100 c. c. of the well-mixed creosote oil is distilled up to 315° , till nothing more passes over; the distillate is well mixed and shaken up with 30 c. c. of a caustic-soda solution of sp. gr. 1.200. The mixture is then boiled, allowed to cool, and again shaken up at least a minute. Then the whole is poured into a separating-funnel (fig. 38). When the two layers have well separated, the caustic liquor below is drawn off and the oil twice more treated with 20 c. c. of soda solution, each time fresh. The three liquors are mixed and after complete cooling are separated from any remaining oil by a separating-funnel, well boiled to remove any traces of oil, cooled, and mixed with about 35 c. c. of dilute sulphuric acid (1 : 3) till the solution shows an acid reaction. The whole is poured into a separating-funnel, where it remains for at least two hours, and the tar-acids are separated from the solution of the salt. The former are now dissolved in 20 c. c. of caustic-soda solution of sp. gr. 1.200 and 10 c. c. of water; the mixture is boiled, filtered through asbestos, the latter washed with not above 5 c. c. of boiling water, and the solution allowed to cool *completely* in a graduated 100-c.c. cylinder. It is now acidified with the same sulphuric acid as before (which will require about 10 c. c.), allowed to stand 2 hours in the cold, and the percentage of crude carbolic acid is read off.

Fig. 38.



Remarks.—Caustic-soda solution of sp. gr. 1.200 is better than weaker liquor, because it separates better from the creosote oil, the tar-acids are precipitated better, and by the smaller quantity of water less phenol is lost. Several treatments with caustic liquor and thorough shaking are indispensable for completely extracting the tar-acids. For precipitating them sulphuric acid is preferable to hydrochloric acid, as the phenols are separated from the solution of sodium sulphate better, on account of its higher specific gravity. Complete cooling is necessary, because otherwise phenols remain dissolved. The application of water must be restricted to a minimum.

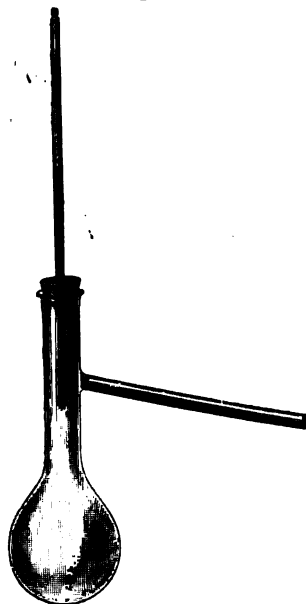
Abel's Process for Estimating the Tar-Acids.

100 c. c. (=104 grams) of creosote oil is distilled at 300°C . The distillate is mixed in a stoppered bottle with 20 c. c. caustic-soda liquor of sp. gr. 1.21, and is shaken up now and then for three hours. The whole is then poured into a burette with a glass tap, which serves as a separating-funnel, a few drops of caustic-soda solution having first been run in to fill the narrow space above the tap. Here the whole is allowed to stand for 12 hours; and the liquor containing the acids is run into a flask provided with a neck 5 or 6 inches long and divided into cubic centimetres, in which afterwards the tar-acids can be collected and their volume read off. The oil remaining in the burette is put back into the stoppered bottle, and is shaken up with another 10 c. c. caustic-soda solution; the solution is added to the first. A little oil comes along with it, which might be removed by agitation with ether; but it is too little to make this worth while. The solution of the phenols in caustic liquor is mixed with dilute sulphuric acid (1 : 3) up to a *faintly* acid reaction, the flask being cooled at the same time. Then enough mercury is poured into the flask to drive all the tar-acids up into its neck, where their bulk can be read off on the graduation.

Fig. 39.

For the purpose of distinguishing carbolic and cresylic acid from the other tar-acids, a certain portion of the acids found before is distilled in an ordinary fractionating-bulb (fig. 39), the thermometer reaching up to the delivery-tube, up to a temperature of 232°C . The bulb is weighed before and after filling and after distillation; the distillate is dried over sulphuric acid. Since phenol distils at 180° and cresol at 204° , the limit of 232°C . is sufficient in any case. Of these two bodies more than half of the tar-acids should consist.

The author would subjoin some remarks of his own. The procedure for the distillation of phenol and cresol from



the other "tar-acids" seems quite illusory, owing to the nature of fractional distillation. This part of Abel's process might be left out, which would simplify it very much, without sacrificing any thing of real value. Otherwise Abel's process seems simpler and less exposed to mechanical losses than Tidy's, because the filtration and the repeated pouring in and out of liquors strongly adhering to the glass, as well as the washing, are avoided. In lieu of the specially constructed flask with a long graduated neck, any somewhat narrow 100 c. c. graduated cylinder, or else a burette, may be employed, and the use of mercury altogether avoided. Tidy's process has the advantage of more certainly avoiding any mechanical admixture of oil with the caustic liquor containing the phenols; whether this causes an appreciable error in Abel's process could only be decided by comparative testing.

According to an observation of C. Weyl (compare next Chapter), it is not advisable to employ a too strong caustic liquor for extracting the phenols.

Carriage of Creosote Oil.

On a comparatively small scale creosote oil is conveyed in wooden casks, which are very liable to leak unless they have been previously washed with a solution of glue. On a larger scale exactly the same contrivances are employed as for tar itself, viz.:—for railway carriage, block waggons with cylindrical or angular wrought-iron tanks holding 8 or 9 tons; for water carriage (on rivers or canals), tank boats.

CHAPTER VIII.

CARBOLIC ACID AND NAPHTHALENE.

CARBOLIC ACID (PHENOL).

For a number of years, ever since the preparation of carbohc acid had become an industry, it had been found suitable not to work for that purpose the whole of the "light oil," but merely the last portion (that between sp. gr. 0.980 or 0.990 and 1.000). Since then the demand for carbohc acid has largely increased, and that for naphthalene has risen to a considerable extent. Consequently all the better factories manage their process so as to obtain a special fraction between that yielding the light hydrocarbons, and the heavy oils, which is specially rich in phenols and naphthalene. We have certainly seen (p. 114 *et seq.*) that this fraction is not made everywhere exactly on the same principles; and its quality at one works will consequently differ a good deal from that at another; but this makes no difference in the manner of treating it to the best purpose, which we shall now describe.

The principle is always this:—treating the oils with caustic-soda liquor, which dissolves the phenols (tar-acids); this solution is decomposed by mineral acids, and crude carbohc acid is obtained; the oil separated from the alkaline liquor is redistilled and yields naphthalene, along with other products. According to whether the fraction has been made sooner or later, the benzene homologues will have to be sought for or the contrary. The crude carbohc acid is partly employed in this state for disinfecting-purposes, and partly sold to those who work it for crystallized phenol &c.

The following is the original process for preparing pure phenol,

by Laurent*, and is essentially identical in principle with that which is even now employed. The fraction of coal-tar distilling between 150° and 200° is treated with a hot saturated solution of caustic potash or soda, some solid powdered caustic potash or soda is added and the mixture well agitated [just in this point, viz. employing solid caustic, the process differs from that now in use; probably at that time, in 1831, the tar did not contain as much naphthalene as now, because the cast-iron gas-retorts then used could not be worked at such a heat as the present fireclay ones; moreover Laurent worked with a comparatively low-boiling fraction, poor in naphthalene]. The oil sets to a crystalline paste; the liquid portion is decanted, and the solid one is dissolved in warm water. Two layers are formed—a light oily one (which is removed), and a heavy watery one (which is saturated with sulphuric or hydrochloric acid). The oil which is formed in the latter process and found floating upon the acid liquid is digested with fused chloride of calcium and fractionally distilled. Thus a white oily substance is easily obtained, which on being slowly cooled yields beautiful crystals.

It has been attempted to cheapen Laurent's process by employing lime in lieu of potash or soda, boiling and strongly agitating. On settling, the neutral oils come to the surface and are removed by decantation; the lime-precipitate is decomposed by hydrochloric acid, and yields phenol. This simple and cheap process, however, does not give a good result; and the treatment with caustic soda is universally preferred, but with a much weaker solution than that prescribed by Laurent. At all events the preparation of perfectly pure crystallized carbolic acid is any thing but simple and easy. It is said that such acid was first made on a large scale by Sell, of Offenbach†; but in any case it was introduced into trade on a manufacturing-scale by the exertions of Crace Calvert and Charles Lowe, of Manchester, who for a considerable time had almost a monopoly of it. Nowadays it is made at other English as well as continental works.

Experience has shown that carbolic acid proper (C_6H_5O) cannot very well be made from the creosote oils distilling above 240° . These

* Ann. Chim. Phys. [3] iii. p. 95.

† According to a private communication from Mr. Brönnert, of Frankfurt, this gentleman as early as 1846 made so-called white limpid ("wasserhelles") creosote, which was frequently refused because in winter it solidified to a white crystalline mass!

always contain tar-acids, but mostly the higher homologues; and the latter are universally admitted to be of great importance in the process of preserving timber; so that it would seem wrong to remove them. We shall therefore not take the heavy oils into account for this purpose. On the other hand, if a "middle oil" has not been collected (from about 170°), in the working-up of the "light oil" (to be described in the next Chapter), considerable quantities of residues rich in phenol and naphthalene are obtained; these are added to the "carbolic oil," and make it about equal to the "middle oil" of other works.

The following are examples of the composition of middle oils (from Stohmann-Kerl, vi. 1179):—

Distilling at	I.	II.	
100°	0	0	per cent.
100°–180°	14.1	9.2	„
180°–200°	41.5	35.2	„
200°–250°	38.7	19.2	„

Watson Smith gives the following results for "light oils" (really equal to "middle oils") from Wigan cannel-coal-tar (compare p. 140):—

Distilling below	Oil of sp. gr. 1.000.	Oil of sp. gr. 1.019.	
170°	10	0	per cent.
180°	5	0	„
190°	12	5	„
200°	22	24	„
	<hr/> 49	<hr/> 29	„

Some recommend redistilling such oils *before* the alkaline treatment, receiving the fraction between 170° and 210° as crude carbolic oil, and running the residue to the creosote oil. But this will cause a considerable loss of phenols*, and it is much more advisable to treat the whole of the middle oils with *alkali*. Even by distilling in a still with a dephlegmator (see below), only part of the naphthalene can be separated from the crude oils; hence it is preferable to effect the first separation by the alkaline treatment. In any case it will be well to let the oil rest for some time, so that as much naphthalene as possible shall crystallize out and can be removed.

* Watson Smith confirms this.

According to E. Waller,* in America the light oil is distilled at temperatures below 177° – 220° ; steam is passed through the distillate as long as it carries away any oils; the distillate ("rectified coal-tar naphtha") is worked for benzol, and the residue ("naphtha tailings") for phenol. If these short hints actually represent the American style of treating the first coal-tar fractions, it cannot be pronounced quite so rational as it might be.

First of all should be ascertained how much alkali the oil requires. It is not necessary in this case to make a formal analytical estimation (of which we shall speak hereafter), but only to find the minimum quantity of alkali required for exhausting the oil. This need only be tested for roughly, in the following manner:—50 c.c. of the oil is put into a 100-c.c. graduated cylinder; and the soda solution is gradually added, shaking after each addition and allowing the liquids to separate. The dark-brown solution of sodium carbolate is distinct from the oil which may be above or below it. The volume of the oil is noted; and if on the next addition of alkali it is not lessened, the last addition must have been sufficient. From this is calculated the quantity of alkali to be used in actual manufacturing-work.

From what we have seen (p. 63 *et seq.*) respecting the behaviour of phenol and cresol to alkalies, we know, first, that true phenol is more easily soluble than its homologues, and hence requires a weaker lye; secondly, that a large excess of caustic liquor reprecipitates the phenols (so that care must be taken to avoid this). Still the margin is so large, that in regular manufacturing-work a test like that just described is hardly required, because there will be no very striking differences in the percentage of phenol. But where unknown oils have to be treated, such a test will have to be applied.

According to Behrens† an important manufacturing "secret" for making crystallized carbollic acid consists in treating the oil with a quantity of dilute soda solution, insufficient for dissolving all the tar-acids; in that case carbollic acid, being the strongest, is first taken up. If at all, this plan is not pursued in the first treatment of carbollic acid, just because there is no certainty here about the quantity of alkali required; possibly it may be done in the subsequent working-up of the crude carbollic acid. Those tar-

* Chem. News, xliii. p. 150.

† Dingler's Journal, ccviii. p. 363.

distillers who only proceed as far as crude carbolic acid (and they are the great majority) see their interest in completely extracting the phenols, and hence will not apply the above-mentioned process.

The following special prescription for the extraction of phenol was given by Charles Lowe, the first manufacturer of the purest crystallized carbolic acid* :—20 tons of gas-tar are introduced into a retort and distilled. The first 200 gallons of "light benzols" are of no use for the extraction of carbolic acid. When that amount of distillate has passed over, the next 600 gallons are collected separately. For each 200 gallons of these oils, having a density of 1.0 to 1.005, 30 gallons of caustic-soda solution of sp. gr. 1.34 are added after dilution to 150 gallons, and the oils are then agitated with the solution for two hours. The mixture is next allowed to settle for four hours, when the alkaline solution is drawn off and neutralized with sulphuric acid. The crude carbolic acid rises to the surface and is skimmed off, and is then allowed to settle in tanks for several days, after which it is ready for casking. The caustic soda used must be free from nitrates.

Here, as we see, rather dilute alkaline liquor is prescribed. In regard to this the following points should be borne in mind. The less pure the oils the weaker should be the caustic solution, if good phenol is aimed at. With crude benzol (which always contains some phenol) stronger caustic can be employed; and the phenol obtained will be still better, though less in quantity, than from carbolic oil. For this reason some distillers do not begin the washing of crude benzol, as usual, with sulphuric acid, but with caustic-soda solution of sp. gr. about 1.200. In the case of "middle" or carbolic oil, such strong alkali would dissolve too much hydrocarbons, especially naphthalene, which would greatly impede the purification of carbolic acid, and might altogether prevent it from crystallizing. Moreover oils are dissolved which have a tendency to turn dark in the air, and thus spoil the phenol. Hence in this case weak alkaline liquors must be employed; and probably Lowe's prescription is more trustworthy than any other, since his interest is to obtain the best quality of crude carbolic acid from the tar-distillers.

Watson Smith takes 33 per cent. by volume of caustic liquor 18° or 19° Tw. for carbolic oil, or 40 per cent. by volume for light oil.

* From Allen's 'Commercial Organic Analysis,' p. 305.

A large South-German manufacturer states * that he obtains crude carbohc acid (with 50 per cent. crystallizable acid) by employing caustic liquor of sp. gr. 1.26, steaming the solution, and decomposing the alkaline liquor by acid. He lays much stress upon the subsequent fractional distillation of the crude acid, but none upon the employment of weak alkaline liquor, or upon fractional saturation (p. 213).

The mixing of carbohc oil and alkaline liquor must of course be done very thoroughly, and with gentle heating, say to 40° or 50°, by means of a steam-coil or jacket. Probably all larger works employ mechanical means for mixing. At some it is done by pumping both liquids continuously backwards and forwards from a lower tank into a higher one and *vice versa*. At others they employ horizontal cylinders covered by a bad heat-conductor, with a longitudinal shaft and agitating-blades. Others employ vertical apparatus, *e. g.* with a perforated piston going up and down†. We shall treat of mechanical mixers more in detail in the 10th Chapter. At some places the agitation is effected by blowing in a current of air, divided by a cross of pipes with many holes, or a perforated plate. This principle has the advantage of dispensing with all working parts within the liquid, and thus being equally applicable for acids and alkalis; the blowing can be performed by the same small blowing engine which is employed at most tar-works for pumping the liquids by air pressure. Fig. 40 shows this arrangement. *a* is a perforated false bottom, which serves for dividing the current of air, blown in through *b*, into numerous jets; *c*, man-hole; *d*, funnel and tap for charging with oil and alkali; *e*, steam-coil; *f*, discharge-cock a little above the bottom; *g*, another discharge-cock in the bottom itself. The air-blast must be so regulated that the liquid shall not be splashed about, but only made to well up thoroughly. A detailed paper on the application of compressed air for the pumping and mixing of liquids has been published by Ramdohr‡.

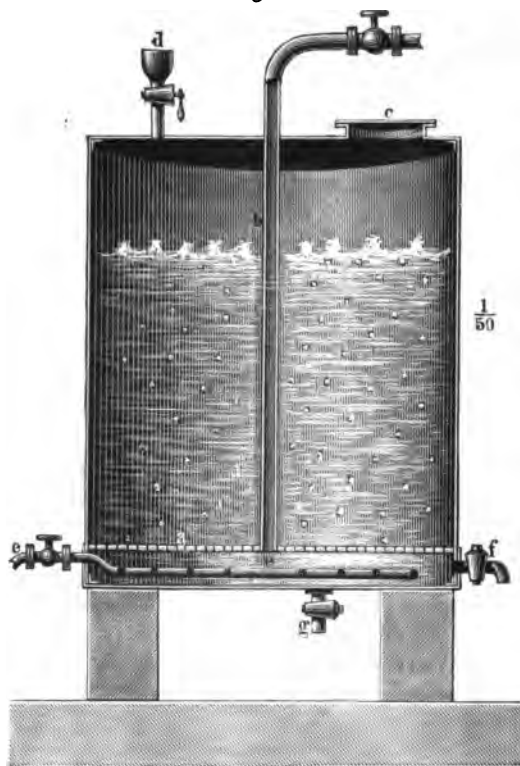
According to Watson Smith, the oil and alkali are mixed up for an hour and a half; the mixture is then tested by mixing, in a 200-c.c. graduated cylinder, 140 c. c. of the alkaline liquor with 14 c. c. strong sulphuric acid, and allowing it to subside; unless

* In a private communication to the author.

† Hübner, Dingler's Journal, cxlvi. p. 421.

‡ Dingler's Journal, ccxvi. p. 158.

Fig. 40.



at least 10 or 12 per cent. crude carbolic acid is found to collect at the top, the mixing should be continued.

The mixing-vessel for this purpose is always made of iron, usually wrought iron, which metal resists the liquor better than any other; the steam-coils, air-pipes, &c. are also made of iron. When mixing by an air-blast, the vessel should be only two thirds full, on account of the welling up. It is mostly closed by a wooden or iron cover, to minimize volatilization. According to the size of the works, the settling (which takes several hours) will either take place in the same vessel, or else the whole contents will be run into a special vessel, placed at a lower level, so that the mixer can be charged again at once. The settling-tank must have two (iron) discharge-cocks, one in the bottom itself (*a*), another in the side a little above the bottom (*b*). The unchanged oil always floats on the alkaline

liquid, which sometimes doubles its bulk and is of intensely dark brown colour. First of all this liquid is run off by the bottom cock (*a*), which is closed as soon as any traces of oil appear. Now the upper cock (*b*) is opened, through which oil entirely free from alkali can be drawn off, whilst between the two cocks a layer of both liquids remains, which is best left behind in the vessel and worked up with the next charge.

As pointed out by Watson Smith, the point at which the alkaline liquid is going to change for the oily one, can be safely recognized by the turbid, milky appearance which sets in.

It is imperative to keep the alkaline liquid as pure as possible from the separated crude naphtha, because even a small admixture of the latter (especially of the naphthalene contained therein) afterwards prevents the crystallization of the carbohc acid. Hence great care must be taken in settling and in drawing off.

The oil drawn off from the liquor (crude naphtha) contains mostly a little of the higher homologues of benzene, but principally naphthalene and other indifferent bodies. If naphthalene is not wanted, it is run to the "light oil" (compare next Chapter) and worked up therewith. Sometimes this does not pay, viz. when the original oil has been collected later on in the distillation; then the residues are run to the creosote oil. Where naphthalene is an object, this oil is by far the best raw material for it, as we shall see below.

The liquor containing sodium carbolate, to which is regularly added that obtained in the washing of benzol and light oil, is now mostly at once decomposed by acid. But some prefer to interpose a special treatment for the removal of impurities. Thus Vincent* adds to the liquor 5 or 6 times its bulk of boiling water, to precipitate the dissolved hydrocarbons. This should not be overdone (compare p. 64); and anyhow the success of this operation will depend upon the fact whether more or less concentrated alkali has been employed from the first. (Vincent starts with concentrated alkali.) Schnitzler† recommends, as extremely efficient, heating the dark liquid in a copper still over a strong fire till the distillate (consisting of water, naphthalene, oils, and phenol) turns milky; the thermometer will then stand at 170°. Most of the phenol remains with the soda as a mass solidifying on cooling. It is dissolved in water in the still itself, and is diluted to three times the

* Payen, Précis de Chimie industr. 6th ed. ii. p. 961.

† Dingler's Journal, ccxiv. p. 86.

original bulk. After some days a mud is deposited, from which the clear liquor is separated. The latter is decomposed by dilute sulphuric acid; and the phenol separated is distilled from a glass retort. After putting aside the water "coming over at first, colourless liquid phenol of honey-like (?) smell was obtained, which solidified on the addition of a small piece of calcium chloride, or a crystal of carbolic acid. The portions passing over last were faintly yellow, and contained more liquid parts. The crystals, after draining them with a Bunsen pump and pressing them between paper, remained white for months in a stoppered bottle in moderate daylight; in an open glass they soon turned pink, and at last deliquesced to a yellow-red liquid. The colour was evidently produced by particles of dust floating in the air" (? See below).

For the large scale Schnitzler recommends a wrought-iron still with a block-tin, lead, or copper worm, and to put a second delivery-tube lower down for use in the later stage of distillation. Insufficiently heated sodium carbolate yields yellow, unpleasantly smelling phenol; it is essential to completely remove the colouring-impurities by evaporation or carbonization &c. An experiment with calcium carbonate did not succeed (perhaps because there was an excess of lime); the mass turned spongy, conducted the heat badly, and retained tarry matters and naphthalene.

Another purifying process is described in Stohmann-Kerl's 'Chemistry'*. The crude sodium carbolate is run into open wood tubs, on whose bottom is laid a steam-coil perforated with many holes. The liquor is moderately warmed; and enough freshly prepared cream of lime is added to make the whole milky white. During this the mass is worked up with a wooden rake; and the heating is continued for 12 hours. After a few hours a skin appears on the surface, which gradually turns into a red foamy scum. It consists of the naphthalene left in the liquor, mixed with lime. It is carefully removed with a perforated wooden scoop, either at once, or at least after the liquor has cooled down. Thus all naphthalene, even to the last trace, can be removed; but it is most essential to keep the heat at the right point. The temperature must never rise so high that the liquid wells up strongly. Perhaps an insoluble compound of lime and naphthalene is formed; but perhaps the action of the lime is only mechanical, the naphthalene being secreted from the alkaline liquor as it is diluted by

* 3rd edition, vi. p. 1181.

the steam blown in. In any case the tubs must be left uncovered and must stand in an unheated room. When the naphthalene has been completely removed and the liquor has been settled, it is carefully drawn off from the lime remaining at the bottom, and is decomposed by sulphuric acid.

Probably all these preparations by dilution, treatment with lime, &c. will be unnecessary, if the carbolic oil be at once treated with *dilute* caustic-soda liquor—say, by Lowe's prescription (p. 214)—because such liquor dissolves less of the hydrocarbons.

Now follows the *decomposition of the alkaline solution of phenols by mineral acid, and the separation of crude carbolic acid*. This operation is generally performed in a vessel lined with lead, which may be provided with a mechanical agitator; but in this case hand mixing is easy and simple. Iron vessels are acted upon too quickly. The acid employed for the decomposition is mostly sulphuric acid. The solution of sodium sulphate resulting from this is probably never utilized as such; and the spontaneously crystallizing Glauber's salt is also of very small value*. If dilute caustic liquor and sulphuric acid of 140° Tw. be employed, but little will crystallize out spontaneously. Some tar-distillers take strong (170°) oil of vitriol; but this is worse than useless, as sulphophenols are formed, which in the subsequent distillation decompose and carry sulphurous acid into the carbolic acid. The addition of the vitriol must be cautiously done, to avoid strong heating, and is only continued till the reaction has become distinctly acid. The men can tell this from the change of colour, without applying litmus paper. According to Watson Smith, 1000 gallons, treated with 400 gallons of caustic-soda solution of sp. gr. 1.090, require about 22½ gallons of sulphuric acid of sp. gr. 1.74.

It has been several times attempted to replace sulphuric acid by the acid refuse from washing the light tar-oils (Chap. X.), after depriving it, by dilution with water, of most of its tarry parts. But it is still very impure; and its use for decomposing sodium phenate has been given up everywhere, as the saving of acid does not compensate for the contamination of the phenol. It is true that another motive was the desire to get rid of that acid refuse; but the proposal of E. Kopp, to combine the employment of this refuse acid for decomposing the sodium phenate with working up

* According to Watson Smith, the crystals always turn blue on standing in the air.

the resulting solution for the alkaloids contained in coal-tar, could never be expected to meet with success, as the quantity of these alkaloids is extremely small, and their mixture most complicated.

According to Watson Smith, in Lancashire even fresh sulphuric acid made from pyrites is not employed for this purpose, but brimstone acid almost exclusively [probably from an unfounded prejudice!]. He further mentions that attempts had been made, but unsuccessfully, to replace sulphuric acid by hydrochloric acid, which is cheaper [and causes less trouble by crystallizing salts]. The alleged reason of this failure is that chlorides of ammonium and amides are formed, which later on are decomposed and act upon the iron of the stills; the ferric chloride distils over, and makes the carbolic acid dark and dirty. Ammonium sulphate produces no such consequences.—But all this must be either a prejudice or else the consequence of unskilful manipulation, since some of the best German works employ hydrochloric acid, and among them are those that turn out the very finest quality of white crystallized carbolic acid.

Lowe and Gill * propose decomposing the alkaline phenol solutions by sulphurous acid. The aqueous solution of the bisulphite is either to be evaporated for crystallization, or employed for preparing sulphurous acid again.

In the place of strong acids, *carbonic acid* can be employed for decomposing sodium phenate. In Scotland this seems to have been done for some years †; Brönnert ‡, of Frankfort, had done it already many years ago. A patent has recently been taken out by Clift § for exactly the same thing. If the decomposition can really be completed without wasting too much carbonic acid, there are considerable advantages gained by this process as against the employment of strong acids. In the former case the soda is not lost, as in the latter, but is recovered as carbonate and can be used over again after causticizing. There would not, as now, be a rather considerable amount of phenol lost, either dissolved or suspended in small drops, in the solution of sodium sulphate or chloride; for as the liquor is causticized and used over again, the phenol would be recovered. No washing of the phenol would be at all necessary as the latter would retain no mineral acids, which probably give

* English patent, No. 1456, 1880.

† Mills, 'Destructive Distillation,' p. 17.

‡ Private communication to the author.

§ No. 967, 5th March 1880.

rise to the formation of traces of rosolic acid (p. 66) and thus turn the carbolic acid red. This, of course, presupposes that the carbolic acid itself is entirely free from stronger acids, which is hardly the case in the ordinary way of working, since even that made from coke or in lime-kilns is contaminated with sulphurous acid. It seems therefore necessary to wash the CO_2 most thoroughly with water, or else to produce it by the action of superheated steam on limestone in iron retorts. Lest too much of it should be wasted, it should be divided into numerous jets by a perforated false bottom or the like, and several vessels should be employed in rotation to utilize the gas methodically, so that the fresh gas (which in the case of lime-kiln gases contains from 25 to 30 per cent. CO_2 by volume) shall always be brought into contact with nearly saturated liquor, and the poorest gas with fresh liquor, on the same principle as that in accordance with which black ash is lixiviated. In this way it has been found possible on a manufacturing scale to completely decompose solutions of sodium sulphide by carbonic acid without employing an excess of the latter*. There would also be this advantage, that, as the carbonic acid need not in this case be free from oxygen, any fire-gases might be used, if well washed: oxygen even acts advantageously here (see below).

After the separation of the crude carbolic acid, the solution of salt, if sulphuric acid has been employed, must be drawn off hot, lest it crystallize in the precipitating-tank. In the case of hydrochloric acid there is no such danger, and more time can be given for the solutions to clear, so that less phenol is lost with the solution of salt. The latter is drawn off by a tap in the bottom, which is shut the moment any carbolic acid appears, whereupon the latter can be drawn off in the pure state from another tap higher up (p. 217). It is preferable to leave the carbolic acid to itself for a day or two to clear, so that the salt-solution suspended in it may completely separate at the bottom: this can be done in a special settler. The longer time is given for the salt-solution to separate from the carbolic acid, the better for the quality of the latter.

In many cases the crude carbolic acid is now sold as such; in other cases it is washed once or twice with water to remove the mineral acids—which, however, is never done completely, because the washings would carry away too much carbolic acid. In any

* This is described in detail in the author's *Treatise on the Manufacture of Sulphuric Acid and Alkali*, Van Voort, vol. ii. p. 352.

case the washings should not be thrown away, but employed for dissolving the caustic soda. The washings are found floating *on the top* of the carbolic acid, and are run off best by a drop-siphon (fig. 41), which can be gradually turned down. This is much more convenient than a common siphon.

Fig. 41.



Sometimes the crude carbolic acid is *distilled* already by the tar-distiller, in order to get it up to the requirements laid down by the buyers (compare below). In that case the fraction distilling between 175° and 205° or 210° is collected as crude carbolic acid. The fraction below this goes to the light oil, the residue to the creosote oil.

Crude Carbolic Acid should have a specific gravity of 1.050–1.065 at $15^{\circ}5$. In the presence of light tar-oils its sp. gr. is often only 1.040–1.045. Its percentage of phenols can be approximately tested (more exact methods will be mentioned below) by shaking it up in a graduated tube with twice its bulk of 9-per-cent caustic-soda solution, added gradually. Hager* recommends an alcoholic solution of caustic potash; Allen prefers the process as described here. The volume of the neutral oils (which may be at the top or at the bottom) is now read off. The separation of the oily and aqueous layers becomes more accurate if (as first proposed by Hager) a quantity of petroleum spirit is added in equal volume to that of the tar-oil; of course this volume must be deducted. This or any similar test cannot possibly be accurate, because the alkaline solution, especially if it be somewhat concentrated, dissolves indifferent oils and naphthalene.

The following prescription for testing crude carbolic acid has been drawn up by Mr. Charles Lowe, and is followed at most English and some continental works. The specific gravity should be between 1.055 and 1.070. One thousand fluid-grains (or say 200 c. c.) of the oil are distilled in a retort, without any special condensing apparatus; and the liquid passing over is collected in graduated tubes. Water first distils, and is followed by an oily fluid. When 100 fluid-grains of the latter have been collected, the receiver is changed. The volume of the water is then read off. If the oily liquid floats on the water, it contains light tar-oil. It should be heavier than water, in which case it may be regarded as

* Wagner's Jahresb. 1872, p. 675.

hydrated acid containing about 50 per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid; and when it measures 625 grains the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 625 grains measure of anhydrous acid contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining its solidifying-point, which should be between $15^{\circ}5$ and 24° . Having ascertained this temperature, a mixture of pure carbolic and cresylic acids is made, in such proportions as to have the same solidifying-point. This must be adjusted by trial; or a series of standard specimens may be prepared. The exact point of solidification can be read more sharply if a minute fragment of crystallized carbolic acid be added, to induce the commencement of the change of state; or the sample may be solidified and the liquefying-point noted. As excess of cresylic acid prevents crystallization, it is evident that in some cases a second fractional distillation should be resorted to, the process being arrested when the thermometer rises to 190° .

Dr. Weyl, of Mannheim, tests crude carbolic acid by a caustic-soda solution of sp. gr. 1.263–1.297. Stronger alkali extracts bodies whose sodium compounds are insoluble in the mixture of liquids, and are precipitated as a heavy layer between the oil and the sodium-phenate solution. These bodies (which have not yet been examined) belong to the heaviest constituents of coal-tar.

Watson Smith supplied the author with the following information. Cresol retains less water of hydration than phenol; hence a superior quality of crude carbolic acid, containing less cresol, gives off more water than inferior. In the former case up to 16 per cent. of water is found. The following are analyses (by Lowe's method) of crude carbolic acid from Manchester and Blackburn tar, both made from Wigan cannel coal.

	Blackburn.	Manchester.	Manchester.
Water (per cent. by volume)	12	13	15
First oil, boiling up to 185° (to be thrown away) ..	11	11	10
Carbolic acid distilling below 190°	48	45	45
" " " " 195 – 196°	$13\frac{1}{2}$	$17\frac{1}{2}$	$17\frac{1}{2}$
Solidifying-point of those $61\frac{1}{2}$ – $62\frac{1}{2}$ per cent.	15°	18°	$16\frac{1}{2}^{\circ}$

He states that 1000 gal. light oil or carbolic oil from Manchester tar yield about 50 gal. crude carbolic acid.

Preparation of pure crystallized Carbohic Acid.*

We have seen on p. 211 that this manufacture is rather difficult, and some of its details are still kept a secret. In the following we shall put together what has been published on this subject, together with some results obtained by Mr. Watson Smith and by the author.

Crude carbohic acid, as supplied by the tar-distillers, contains cresols, water, naphthalene, resinous matters, &c. The easiest to remove is the *water*; by mere distillation most of it is expelled at 100°; and the boiling-point then rises rapidly, so that at 180° anhydrous phenol passes over. Still more safely, the raw product, first freed from most of its water by distillation, is digested with fused calcium chloride and then drawn off from it (not distilled over it, since in that case the CaCl_2 would again give up some water). Bickerdike † recommends distilling over 1 or 2 per cent. dehydrated cupric sulphate, which can always be recovered. Exactly the same service is done by 1 or 2 per cent. of concentrated sulphuric acid (see below).

The *distillation* usually takes place in cast-iron or wrought-iron stills holding only 150–200 gallons, of moderate depth, so that the vapours are carried away more readily. The heating is mostly effected by a direct fire, with a protecting arch; but it can also be done by an oil-bath, or by superheated steam in a lead coil. Others recommend copper stills, which are especially adapted for the distillation over sulphuric acid, with or without potassium bichromate (see below). The stills are in every case provided with a thermometer, whose mercury vessel is placed opposite the vapour-delivery tube and whose scale projects outside. The worm is best made of zinc (see below).

Watson Smith recommends luting the man-hole cover with a paste of a solution of glue and partly slaked quicklime. The author would prefer asbestos packing.

In distilling, the following fractions are made. First is collected what distils below 180°; this is mostly water and hydrocarbons floating on the top of it; but it already contains some phenol, and is hence kept in order to be redistilled. The second fraction, from 180° to 205°, is put aside for crystallization; the still-residue either

* See, for its properties, p. 59 *et seqq.*

† Chemical News, xvi. p. 188.

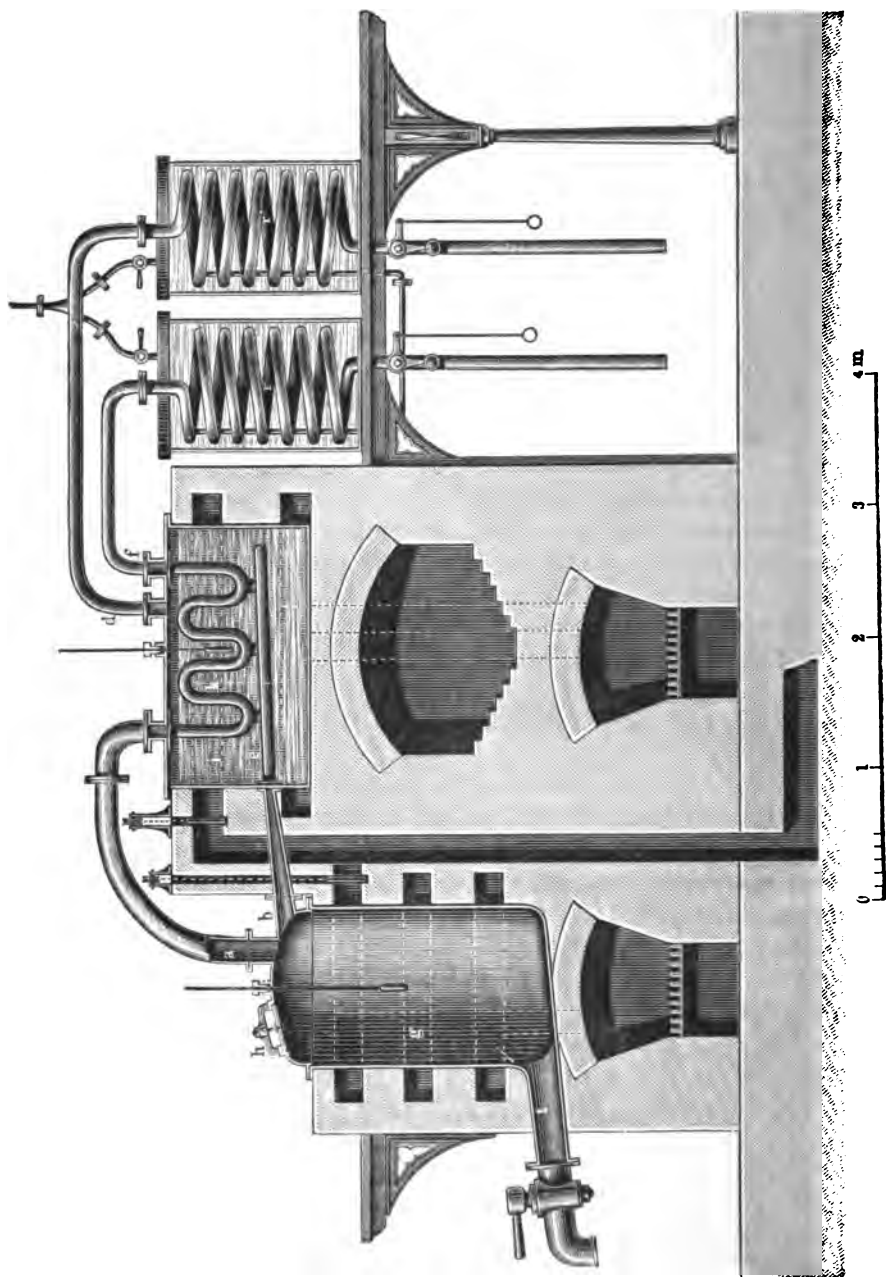
goes to the creosote oil, or is rectified once more, in order to collect the distillate below 205° ; or else it is once more treated with alkali, &c.

The above-mentioned principal fraction is left to crystallize in a cool place (at about 8° or 10° for instance), in large funnel-shaped vessels with a tap below, through which afterwards the mother liquor can be drained away. The latter is a solution of phenol in cresol, and is redistilled. Its draining from the crystals may be facilitated by a centrifugal machine. The above low temperature will be obtained during the summer season sometimes by circulation of cold water, sometimes only by a freezing-mixture.

If this fraction should refuse to crystallize (which will happen if it contains too much cresol), it must be rectified and the distillates from 175° to 185° , from 185° to 195° , and from 195° to 205° collected separately. The first and last fraction are redistilled when enough of them has accumulated; the middle fraction (from 185° to 195°), which is no doubt obtained again, is united with the former. It is evident that no general prescription can be given, but that the fractions, which may become very numerous, must be grouped as they belong together, so as to separate the homologues and ultimately get the boiling-points to be constant within a few degrees, viz. $184-188^{\circ}$ for carbofic acid and $200-203^{\circ}$ for cresylic acid. The ordinary crystallized phenol boils at 186° ; if the purest, boiling at 182° , is aimed at, the thermometer must be observed accordingly.

Instead of making such a complicated series of rectifications and groupings of the fractions, it is evident that the principle of *dephlegmation* or *separation* is the proper one to employ here as well as in the rectification of spirit of wine, or in that of benzol, where Mansfield employed it a generation ago. It consists in *partially* cooling the vapours, so that the less volatile bodies are condensed and flow back into the still. This principle can be applied in very different ways. We shall see in Chapter X. how this is done for benzol; here we will only describe the apparatus constructed by Girard for the separation of aniline and toluidine, which must be suitable for phenols as well, because their boiling-points very nearly agree with those of the amides. In fig. 42, *g* represents a still with discharge-pipe (*d*), man-hole (*h*), thermometer, vapour-delivery pipe (*a*), and a pipe (*b*) for running back the liquid that comes from the separator (*k*). This separator, formed of lead pipes, is

Fig. 42.



placed in a trough, *i*, filled with pure phenol or with oil or paraffin, heated by a separate fire and covered by a lid in which is fixed a thermometer and a pipe, *d*, which, when phenol is employed, leads to a worm, *r'*, or, in the case of oil or paraffin, into a chimney. The separator itself is connected by *f* with another worm, *r*.

When the still, *g*, is fired, the vapours pass into *k*, and heat the contents of *i* to the boiling-point of phenol. This is hastened by first heating up *i* nearly to that point. The phenol vapour given off in *i* is condensed in the worm *r'*. The vapours passing through the bends of *k* are here separated into a liquid portion, essentially cresol, which collects below in *e* and runs back to *g*, and vapour of pure phenol, which condenses in *r*. When all the phenol has passed over, the cresol, if required, can likewise be obtained pure, *i. e.* free from less volatile products; but in that case *i* must be filled with oil or paraffin, and heated to 201°.

Girard's apparatus could be improved by bending the connecting-pipe *b* so as to make an hydraulic lute, and thus prevent the vapours from passing at once to the back part of *k*. Its action would even then be hardly so perfect as that of the more modern column apparatus, which will be described in the 10th Chapter.

It would appear that in crude phenol occur oils which are modified by oxygen and yield brown or red resinous products. Moreover, as we have repeatedly pointed out (pp. 66 & 220), there is occasion for the formation of rosolic acid, likewise on condition that oxygen be present. This agrees with an observation made by Hager*, according to which white phenol is turned red by traces of ammonia; for the latter yields a red salt with rosolic acid. If really, as Hager assumes, ammonium nitrite is the agent in this case, the nitrous acid will furnish the oxygen. Hence the colouring-matter will be kept out of the finished phenol, if from the first enough oxygen is supplied to complete the oxidation before the pure phenol is distilled. Upon this is based, among others, the process of H. Müller†, who at the same time introduces fractional precipitation (analogous to the fractional saturation mentioned by Behrens, p. 213) of the crude carbolic acid before distillation. The alkaline carbolic liquid contains, besides carbolic acid, some oxidizable bodies which give rise to a brown coloration, and also, especially in concentrated solutions, a considerable

* Pharmaceutisches Centralblatt, 1880, p. 77.

† Dingler's Journal, clxxix. p. 481.

quantity of naphthalene and other indifferent substances insoluble in water by themselves. It is diluted with water till further addition precipitates no more naphthalene *; the dark brown liquid is exposed to the air in a shallow vessel for several days, with frequent stirring; it is then filtered, its percentage of phenols ascertained, and the quantity of sulphuric acid necessary for precipitating the whole of them calculated. If now only $\frac{1}{4}$ or $\frac{1}{3}$ of the calculated acid is added with frequent stirring, at first the resinous substance, changed by the action of the air, is precipitated, mixed with more or less of the phenols. A further addition of acid precipitates essentially cresol; and after a few trials almost pure phenol, crystallizing after a single distillation, can be obtained by the third and last precipitation. In order to remove the water, a current of dry air is passed over the phenol heated almost to boiling. The aqueous vapour is usually accompanied by an unpleasantly smelling substance, according to Müller a sulpho-compound of phenol, which can be removed by adding a little lead oxide before distilling. (Such sulphur compounds no doubt exist already in the tar; but they may also be formed afterwards by incautious precipitation with strong sulphuric acid, as pointed out p. 219.)

The exposure of the liquor in shallow pans with frequent stirring, recommended by Müller, would no doubt be advantageously replaced by forcing in a finely divided current of air, or by running the liquor down a coke column, &c. The same object is attained † by adding $\frac{1}{2}$ or $\frac{1}{3}$ per cent. potassium bichromate, and the sulphuric acid necessary for decomposing this, to the crude carbolic acid in the still, and heating gently at first. If this does not suffice to make the phenols distil colourless, more bichromate must be added.

According to the author's experiments it is true that even on a small scale, from carbolic acid which, in spite of being dehydrated by calcium chloride and properly fractionated, could not be brought to crystallize, a good white crystallizing product was obtained when it was distilled over a little potassium bichromate and the corresponding quantity of sulphuric acid. This product fused at 35° , i. e. several degrees above phenol which had been treated exactly

* This point is not very easily hit; hence it is preferable to employ dilute alkali from the first, as already pointed out.

† Stohmann-Kerl's 'Chemie,' vi. p. 1182.

in the same way, but leaving out the bichromate and employing only 2 per cent. of concentrated sulphuric acid. No doubt a still higher fusing-point would be attained in operating on a large scale.

By the methods just described it is easy to obtain crystallized phenol, but scarcely in the perfectly pure state—certainly not such as will remain white. The distillation in metal stills must in any case be followed by rectification of the crystallized phenol in glass retorts, or in a copper retort with a porcelain or silver head and an earthenware or silver worm. Base metals must be strictly avoided in this last distillation, because the smallest trace of copper, iron, or lead &c. colours the product. The condensate is received in glass bottles and is poured into the tin boxes intended for sending out, which are closed except a small opening for inserting a funnel. After standing a few days, crystallization sets in of itself, or is induced by a shock. The mother liquor is now drained off, the box being turned upside down; fresh carbolic acid is then run in, which will crystallize quickly; the mother liquor is drained again; and this is continued till the box is quite filled with crystals, whereupon the opening is closed.

Even in this way carbolic acid remaining white in the air and the light will not always be obtained; sometimes the acid is discoloured even from the first. Hence, before making the last rectification, it should be ascertained that the phenol intended for it does not become discoloured on standing. If it does so, it must be further purified in one of the ways indicated.

For the following detailed and reliable description of the manufacture of pure carbolic acid, as carried on in Lancashire, the author is indebted to Mr. Watson Smith:—The crude carbolic acid is distilled in cylindrical wrought-iron stills 2 feet 9 inches wide, 2 feet 2½ inches high, with a head 5½ inches wide and a thermometer. The worm should be made of zinc—lead, copper, and tin having each been tried and failed. Three different fractions are made:—first, water, with some oil; second, good, crystallizable oils; third, oils not crystallizing, containing cresols and naphthalene (compare Lowe's prescription, p. 222). If the crude phenol be good, the second fraction will crystallize on standing. It is well agitated with some highly concentrated and pure sulphuric acid, in the proportion of 1 part acid to 50 parts of phenol by weight; with inferior phenol, 2 parts acid to 50 phenol may be used, but never more: and only one such treatment must be employed; otherwise the oils

will not crystallize afterwards. In this process the phenol deepens in colour, turns pink, and becomes perceptibly warm. The mixture, well agitated, is poured *at once* (this is very essential!) into the still, and distillation commenced and carried through without stopping and starting again. The first products come over between 150° and 160° C.; and the distillate often crystallizes immediately after dropping. Not much comes over below 175°; and it is better to keep this separate. Usually most comes over between 175° and 185°. At this stage the contents of the retort commence to coke, and the process is stopped. The contents of the receiver are let stand for several hours, to cool completely and crystallize. The mass obtained is set to drain for two or three days, the more thoroughly drained upper portions being from time to time removed. To a portion once crystallized no fresh distillate must ever be run, as it would dissolve some of the crystals again. Care must be taken not to crush the crystals. The oil that drains from them is technically termed "phenylene." This is again distilled and more crystals obtained from it, which are drained; and the resulting "phenylene" is distilled a third time, but without further treatment with sulphuric acid. In distilling the "phenylene oils" it is usual to leave in the retort $1\frac{1}{2}$ gallon (sometimes 2) out of every 20, this residue being technically termed "terebene." It is assumed that the latter contains the oils which would prevent the phenol from crystallizing. When the "phenylene" has thus been exhausted by two or three distillations, it is set aside as "bad phenylene."

In lieu of these repeated fractional distillations it has been found advantageous to artificially cool the "phenylene oil" by refrigerating machines. [That actually employed in England is the ether machine (probably Harrison's or Siebe's); but it is well known that Linde's ammonia machine is the best refrigerator constructed up to this time.]

All the drained crystals obtained as above mentioned are now fused on a water-bath; the liquid is poured into an iron retort with a zinc worm, and distilled—the first small portion (containing water) being rejected, and most of the remainder received into bottles or other vessels, where it solidifies quickly on cooling, forming a white crystalline mass which is sold as "pure commercial carbolic acid." The small quantity left in the retort is classed as "terebene oil." A purer product than the above is obtained by placing the bottles upside down for a day, re-fusing the drained mass on a water-bath,

and pouring it into fresh, perfectly clean and dry bottles or other vessels. The liquid now sets perfectly hard and very white, and is termed "finished commercial carbohc acid."

For "finished medical carbohc acid" the first crystals obtained from "phenylene oils" by draining all night are melted into a glass retort, and a little of a mixture of equal parts of sodium bicarbonate and pure litharge or red lead, well mixed and pulverized, is added. A very small quantity suffices; the lead oxides probably act in retaining sulphur compounds. After standing for some time, distil into a clean dry vessel, rejecting the portions first coming over, which contain some moisture. The crystals obtained are fused on a water-bath; and the resulting liquid is poured into clean dry bottles, in which, on cooling, it forms pure white and solid crystallized carbohc acid.

The *yield* of pure products from crude carbohc acid is shown in the following table, taken from Kerl-Stohmann's 'Chemie,' vol. vi. p. 1184.

Source of the tar.	Nature of the starting material subjected to the alkaline treatment.	Pure product boiling between 183° and 203°.	Crystallized carbohc acid obtained therefrom.	Liquid carbohc and cresylic acids.
		per cent.	per cent.	per cent.
South Germany.....	Light oil.	34·7	13·1	21·6
Ditto	Oreosote oil.	44·8	44·8
Saxony	Light oil.	33·1	13·9	19·2
Saxony, Rhineland, Vienna	?	30·4	6·0	24·4
Sundry	Light oil.	43·7	29·8	13·9
South Germany and Saxony	Light oil.	41	28	13

The considerable loss which takes place in the working-up of crude carbohc acid is caused by its percentage of empyreumatic products, neutral hydrocarbons (especially naphthalene), tar-acids boiling above 203°, and working-losses.

According to Wurtz*, sundry tars contain the following quantities of "phenol" [which probably means all "tar-acids"].

Tar from Wigan cannel coal...	14	per cent.
„ Staffordshire „ ...	9	„
„ Newcastle „ ...	5	„
„ Bog-head	5	„
„ certain kinds of peat	15-20	„

The German tars yield on an average 5 or 6 per cent. of phenols, of which about one third are crystallized carboic acid.

Estimation of Carboic Acid.*

It is estimated most accurately as *tribromphenol*, which is quantitatively precipitated from phenol or its solutions on addition of bromine-water. It appears as white star-shaped groups of needles, of peculiar smell, fusing at 95° , insoluble in water, acids, or somewhat dilute alcohol, soluble in alkalies, ether, or absolute alcohol. Hence it is only necessary to acidify the phenol or its solution in water or dilute alcohol, and to add bromine-water till the liquid has assumed a permanent yellow colour. It is best to heat the liquid till the precipitate fuses to an oil, and then to cool it; the product will thus solidify to a cake, which is easily washed, dried, and weighed. If much cresol has been present (which also gives a tribrom-derivative, but a liquid one), the precipitate is a sticky mass. 100 parts $C_6H_3Br_3(OH)$ correspond to $28.4 C_6H_5(OH)$.

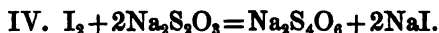
Instead of weighing the tribromphenol, which is difficult, as that substance is rather volatile at 100° , it can be accurately estimated volumetrically†. Allen proceeds as follows:—A certain weight of the sample is dissolved in water; as much as corresponds to 0.1 of the original substance is taken out and put into a stoppered bottle holding 250 c. c. Further, to 7 c. c. of standard soda-solution (=0.040 gram NaOH per litre) bromine is gradually added till a yellow colour appears and remains; the liquid is then boiled till it has become colourless again. It now contains 5 molecules of sodium bromide and 1 of sodium bromate. When completely cooled, it is put into the phenol-solution, after which 5 c. c. concentrated hydrochloric acid is at once added, and the bottle stoppered and shaken for some time. The reactions are:—

* The methods of approximately testing crude carboic acid are given in p. 222; the qualitative reactions in p. 61.

† Koppeschaar, *Zeitschr. f. anal. Chemie*, 1876, p. 233.



The bromine set free in the first, and not fixed by phenol in the second reaction, must be still free, and is estimated by adding potassium iodide and titrating the iodine liberated by a decinormal solution of sodium thiosulphate:—



For this purpose the bottle is allowed to stand for 15 or 20 minutes, a solution of about 1·25 gram potassium iodide (free from iodate) is added, the bottle is stoppered, shaken up, and allowed to rest. Its contents are now poured into a beaker; the bottle is rinsed out, a little starch-solution is added, and decinormal thio-sulphate is run in from a burette till the blue colour is gone. [It will be best not to add the starch till the colour of the liquid has diminished to light yellow.] The calculation is made as follows:— 7 c. c. of normal soda-solution neutralize 0·560 gram of bromine, all of which is liberated by hydrochloric acid. 0·1 gram phenol would require 0·4068 and leave a surplus of 0·1532 gram; the latter would liberate enough iodine to saturate 19·5 c. c. of decinormal thiosulphate. Every cubic centimetre of thiosulphate used over and above this indicates 0·00197 gram impurities in 0·1 gram of the sample—that is, 1·97 per cent.

Koppeschaar originally employed a bromine-solution of unknown strength, and ascertained its percentage by titration with potassium iodide and sodium thiosulphate. Since this dispenses with preparing a fresh bromine-solution every time (as prescribed by Allen), the original process is undoubtedly preferable if many estimations have to be made*.

Degener† titrates with freshly prepared bromine-water, employing, as indicator of the excess, starch-paper soaked with potassium iodide.

Leube‡ describes a colorimetical test with ferric chloride, which can only yield approximate results.

Nietsch§ recommends converting the phenol into a sulphonic

* Compare also Waller, *Chem. News*, xliii. p. 152.

† *Journ. f. prakt. Chemie* [2] xvii. p. 390.

‡ *Dingler's Journal*, ccii. p. 308.

§ *Wagner's Jahresh.* 1879, p. 1036.

acid, preparing its barium or lead salt, and estimating barium or lead by sulphuric acid. This process cannot be accurate, because there is no certainty that only monosulphonic acid will be formed.

In any case it must be borne in mind that *cresol* gives exactly the same reactions as phenol, and the quantity of bromine which indicates 1·000 phenol would indicate 1·106 *cresol*.

Applications of Carbolic Acid.

In the pure state phenol is employed in the manufacture of artificial colours, especially of picric acid and corallin. Also some azo-colours have been made with it; and undoubtedly many other applications of it and its homologues will follow in this line; but it is very doubtful whether it will ever pay to employ phenol as a starting-point for preparing rosaniline, as has been proposed.

Most of the carbolic acid is used for antiseptic purposes. For disinfecting sewers, stables (in the case of cattle-diseases), or even human dwellings, the cheaper descriptions, which are liquid and contain *cresol*, are probably as valuable as crystallized phenol, and also for preserving hides, bones, &c. for sea carriage. The preservation of wood by pickling with *cresote* oil is founded, at least partially, on the same principle. The preservation of meat in the same way has often been proposed, but does not appear to be practicable, owing to the very tenaciously retained smell and taste of carbolic acid. The latter has also been proposed for preserving beet-root juice*.

For medical purposes, especially for internal use, as well as for Lister's antiseptic treatment of wounds, and for cleaning the instruments, hands, and clothes, the purest crystallized acid is always preferred, both on account of its higher solubility and of its less unpleasant smell, which can be entirely masked by a little oil of geranium†. Touching its solubility, some phenols of lower melting-point are more soluble than others of higher melting-point—evidently because the lowering of the melting-point was caused more by the presence of water than of *cresol*. The usual requirement is that 1 part of phenol should give a clear solution with 19 parts of water.

Crude sodium carbolate is employed as a protection against dry rot, under the name of "house-preservatory."

* Cunisset, Bull. Soc. Chim. 1874, xxi. p. 47.

† Compare what is said on the solubility and other properties of pure phenol in Chapter II. (p. 59 *et seq.*).

Carbolic-Acid Preparations.

These are mostly mixtures of crude carbolic acid with lime, frequently of but little value as disinfectants. We shall enumerate only a few of them.

Macdougall's Disinfecting Powder is a mixture of crude carbolic acid with impure calcium sulphite (made by passing sulphur dioxide over heated limestone).

Calvert's Carbolic-Acid Powder is a mixture of carbolic acid with the siliceous residue from treating china-clay with sulphuric acid (in the manufacture of patent alum). It ought to contain from 12 to 15 per cent. of carbolic acid: but the percentage is often far below this; it is ascertained by distilling, say, 100 grams in a glass retort. The distillate is partly oily, partly aqueous. The oily portion ought at least to be tested with caustic-soda solution (p. 64), since it generally contains valueless indifferent tar-oils. The phenol contained in the aqueous portion can be estimated by bromine-water. Disinfectants containing lime should be slightly acidified before distillation.

Quite recently Messrs. C. Calvert & Co. have manufactured also a 50-per-cent. preparation in tablets*.

Sivern's Disinfecting Mass† consists of lime, magnesium chloride, and tar, and only indirectly belongs to this class.

Carbolic-acid Soap ought to contain 10 per cent. of carbolic acid, but loses some of it in the course of time by evaporation. The cheaper descriptions contain mostly cresol. The phenols can be estimated by dissolving 10 grams of the soap in 100 c. c. of hot dilute soda-solution, adding 100 c. c. of saturated solution of common salt, heating again, and allowing to cool. The salted-out soap is filtered and washed with salt-solution; in the filtrate carbolic acid is estimated by the bromine process, described p. 232‡.

Holtz's Phenolith§ is made by dissolving anhydrous boric acid in phenol or cresol, which take up about 40 per cent.; the mass forms a stiff paste, and can be converted into a powder by adding a little common salt, borax, or saltpetre.

* Chem. News, xl. p. 38.

† Compare Schrader and Berens, Wagner's Jahresb. 1871, p. 702.

‡ Compare, as to the details of some of these testing-processes, Allen's 'Commercial Organic Analysis,' vol. i. p. 312 *et seq.*

§ German patent, No. 6498.

NAPHTHALENE*.

Large quantities of crude naphthalene are obtained by simply allowing creosote oil to cool down, especially by collecting its first portions till the point is reached at which a sample does not show any crystals when run on a cold iron. The crude naphthalene is separated by filtering or pressing, but is difficult to purify; and this process will probably be more extensively employed only when the demand for the article increases much more. Probably a first purification would be best effected by washing with solvents, or by recrystallization from light tar-oils, petroleum spirit, or alcohol. An indispensable condition would be the most perfect possible recovery of the solvent.

Most pure naphthalene is now made from the same oil that serves for preparing phenol, viz. from the residual oil remaining after the alkaline treatment. This is decidedly rational, as thus one of the expensive purifying agents has been applied beforehand to another purpose. Indeed, when the oils drawn off from sodium carbolate (p. 217) are distilled in the light-oil still (see next chapter), at first a little light oil passes over, but afterwards almost pure naphthalene. This is seen on mixing a sample of the distillate with cold water, when no more oil collects on the top, but white crystallized masses float all over the water. The receiver is now changed, and the distillation is continued with the precautions to be described below for preventing any choking-up. The receiver contains a white crystallized magma, from which, after cooling, the naphthalene is separated by pressing. The first pressing can be done in a filter-press, the second in an hydraulic press. By recrystallizing from alcohol and subliming, the naphthalene might be still further purified; but that would be too expensive.

This first distillation is often omitted, and the naphthalene obtained only by allowing the liquid to cool; but then much less is got, a good deal remaining dissolved in the liquid portion.

Usually the crystallized naphthalene (which in spite of the oils being pressed out, quickly reddens in the air) is chemically washed. This is more easily effected if the naphthalene be treated soon after pressing, before the adhering oils have been changed by the air. The colour may arise from the formation of rosolic acid from adhering traces of phenol (p. 66), or from oxidation of empyreu-

* Properties, see pp. 46-48.

matic resins ("Brandharze"). When once the oils are removed, it is all the better if the air thoroughly acts upon the naphthalene and colours it *before* the chemical washing and distillation.

The washings, if the oils have not been previously submitted to an alkaline treatment, must begin with this. The caustic liquor may be of any convenient strength. The treatment is effected in closed iron vessels, heated above the fusing-point of naphthalene (79°) by a steam-jacket or a coil, and preferably provided with a mechanical agitator. With very impure naphthalene this treatment should be repeated. In any case the fused naphthalene must be mixed up for some time with the liquor; and after the latter (which collects at the bottom) has been run off, the naphthalene must be washed with hot water, which will now rise to the top.

With better crude naphthalene, especially that distilled in the manner mentioned in p. 236, the alkaline treatment may be dispensed with, and the washing begun with sulphuric acid, which in the concentrated state removes the residual phenols in the shape of sulphonic acids. Vohl* recommends sulphuric acid of 45° Baumé (=sp. gr. 1·453). According to the author's experience this is too weak; acid of at least 1·700 sp. gr. should be employed. The strongest vitriol, of sp. gr. 1·84, is even better; but at that temperature it dissolves much naphthalene, so that less, though of a better kind, is obtained. On the large scale 5 to 10 per cent. of acid will suffice.

The mixture with sulphuric acid takes place in wooden or iron vessels lined with lead, heated by indirect steam and provided with an agitator: the subliming of naphthalene during this operation is a little troublesome. Now follows washing several times with water and at last with weak alkaline liquor, to remove all acid, and finally distillation (see below).

This process, however, does not render the naphthalene perfectly pure; after some time, even when properly distilled, it still turns pink in the air. But the object can be attained in this way:—Starting from the assumption that this pink colour is caused by the formation of rosolic acid from traces of phenol, or at all events from some oxidation, the author in treating with acid (vitriol of sp. gr. 1·70 or 1·84) added a small percentage of artificial manganese dioxide ("Weldon mud"), and on distilling obtained a product which has remained perfectly white for a full year, whilst the best

* Journ. f. prakt. Chemie, cii. p. 29.

samples of commercial "purest" naphthalene placed beside it have turned pink. Probably other oxidizing agents would do the same service*.

In order to see at once whether a sample of naphthalene will turn pink or not, tests are made with sulphuric and nitric acids. On dissolving the sample in pure hot concentrated sulphuric acid the latter should only turn faintly purple or pink; the author has never yet met with a sample which left the acid entirely colourless when dissolved in somewhat large quantity. Even the best commercial brands sometimes turn the acid pretty strongly red. The other test is made by pouring pure, *not* fuming, nitric acid on the bottom of an exsiccator and placing the naphthalene in a watch-glass above it, covering up the whole as usual. If the sample remains white for half an hour, it is good, and if for two hours, it is excellent. Inferior descriptions soon turn pink. After some hours all samples turn yellow, probably owing to the formation of nitronaphthalene.

The washed naphthalene is now either sublimed or distilled. The *subliming* can be done on a moderate scale in the apparatus fig. 43 (taken from Wurtz). *a* is a pan for melting the naphthalene, heated by the fire on the grate *b*; *c* is the snore-hole; *dd* are flues. The pan is covered by a tub, *f*, hung by chains from a small crane *e*; in its top there is small air-vent. The naphthalene sublimes into the tub, forms crusts on the sides, and is knocked out at the end, after moving the tub sideways. The fire should not be so strong that the naphthalene can melt in the tub and run back into the pan.

The apparatus fig. 44 is intended for a larger scale of working. *a* is a shallow iron pan, say 10 feet \times 7 feet \times 3 feet deep. The steam-coil *b* on its bottom serves for heating. The pan is covered by the slanting wooden roof *c*, whose lower part can be turned back into the position shown by the dotted lines. To this is attached a wooden chamber, *d*, say 16 \times 10 \times 5 feet, with a working-door, *e*, and a flap on the top, serving as safety-valve. The heat of the "dry" steam in the coil *b* suffices for subliming the naphthalene; it should not go so far as to give rise to distillation. The naphthalene collecting in *d* is taken out at intervals of a few days.

Some state that it is better to mix the naphthalene with sand before subliming; but this seems to be quite unnecessary.

It has also been attempted to effect the sublimation by blowing

* Chem. News, xliv. p. 65.

Fig. 43.

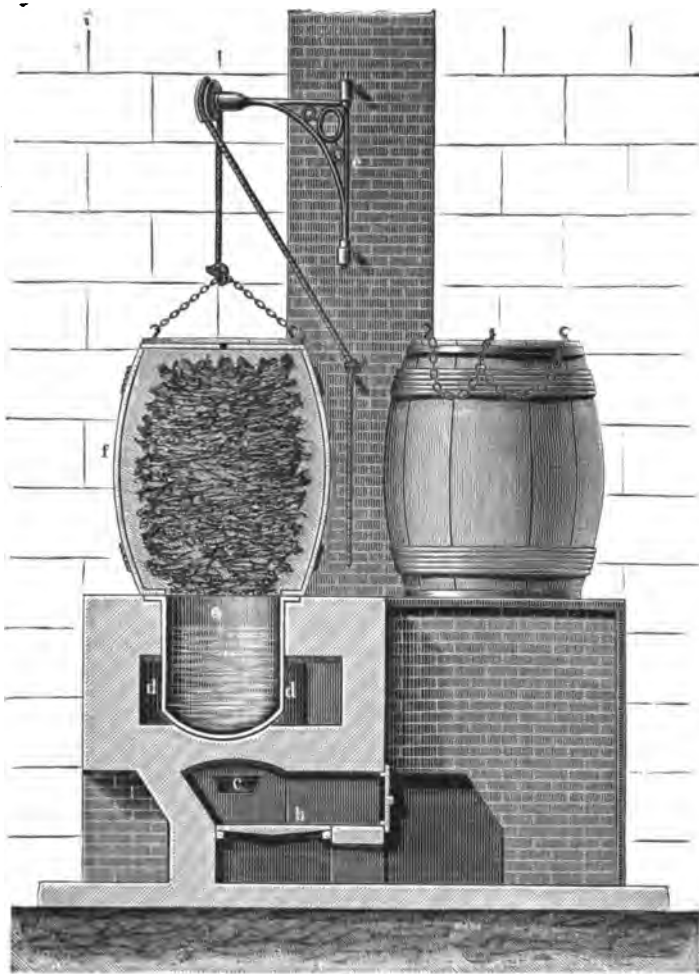
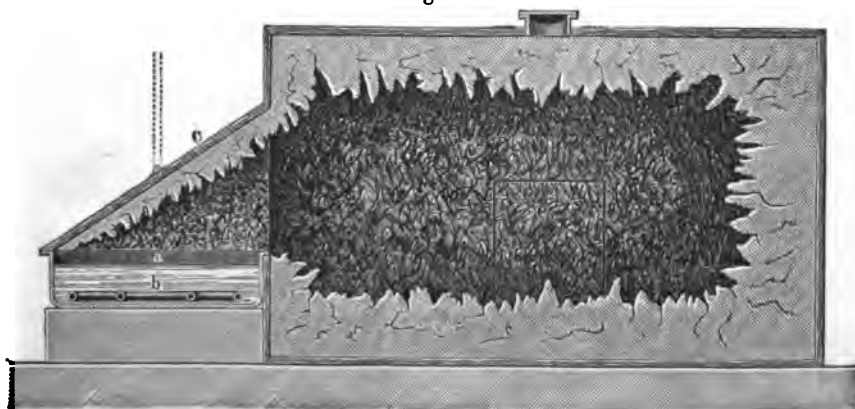


Fig. 44.



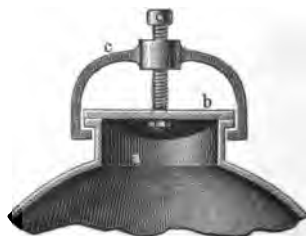
in hot air by means of a fan-blast; but this has been given up again. Ordinary air easily produces a fire; and a previous removal of the oxygen by live coals is too expensive. Moreover the condensation is more difficult than when the heating is produced by indirect steam.

Much preferable to sublimation is the *distillation* of naphthalene, both because it permits larger quantities to be dealt with and because fractionation is in this case much more easily effected. It would appear that all the factories that turn out the best naphthalene distil it. The stills are shallow wrought-iron vessels, holding a ton or upwards, heated by a direct fire, but protected against its first action by a curtain arch; they are provided with a man-hole, a safety-valve, and a very high head (up to 7 feet), which can be furnished with contrivances for dephlegmation, but which already acts in this direction by the cooling effect of the air.

The condensation is effected either by a simple iron worm similar to those used for tar—but with the water in the tub always kept at 80° at least, and sharp elbows and the like (where at the end of the operation solid naphthalene might accumulate and cause in the next operation a dangerous tension in the still, or ultimately an explosion) being avoided. If after all a plug of naphthalene should choke up the worm without its place being noticed at once (in which case it could be melted by boiling water), the safety-valve will blow out. This is a signal for instantly drawing the fire; in the worst case the still must be cooled from above by pouring water upon it.

In lieu of an ordinary safety-valve (which easily gets fast, and anyhow might not act quickly enough), a contrivance like that shown in fig. 45 may be advantageously employed. Upon the still is fixed a flanged pipe, *a*, 12 inches wide, covered by a metal plate, *b*. Hemp packing, and the weight of *b*, suffice for keeping the joint tight without screwing down the arm *c*. The latter is quite loose; and its only object is to prevent the cover *b* from being violently jerked away whenever it is lifted by excessive tension in the still. *b* will then be lifted as far as *c* allows it, and will permit the vapours to escape.

Fig. 45.



Some manufacturers, in order to avoid any danger of choking up, work without a worm, with an apparatus like that shown in fig. 46. The vapours pass through the tube *a*, kept warm by the

Fig. 46.



steam-pipe *bb*, into the wrought-iron cylinder *d*. Opposite *a*, running in the same slanting direction, is a pipe, *c*, through which the steam-pipe *b* comes out. Thus *a* is prevented from being choked up; and *c* also serves for an occasional cleaning-out. *d* is placed to two thirds of its height in a wider cylinder, *e*. If the cooling effected by the outer air is not sufficient, water is run upon *d*, which collects in the outer cylinder and runs away. But the temperature in *d* is kept high enough for the naphthalene to remain liquid and to run out through the pipe *e*. It is collected in shallow iron dishes, where it solidifies into cakes, which are either broken up and packed at once, or once more subjected to hydraulic pressure.

In distilling, first of all a little water and light oil appears. When the thermometer (in the vapour) has risen to 210° , the receiver is changed and pure naphthalene collected up to 230° , or even 235° . Then either the still is stopped and the residue run to the creosote oil, or the distillation is continued into another receiver, and the impure naphthalene collecting there is again purified. Apart from the danger of choking up, the distillation is easy and quick.

Instead of being broken into pieces, the naphthalene is sometimes cast into rolls, like those of brimstone, for the "albo-carbon light." This is done by means of hard-wood moulds, wet inside and a little tapering to facilitate the getting-out.

Employment of Naphthalene.

Formerly naphthalene was one of the least welcome constituents of coal-tar. It occurs in all kinds of coal-tar, generally up to 5 or 10 per cent. by weight, sometimes perhaps even in excess of that *. It ultimately accumulated in the creosote oil and caused inconveniences by crystallizing there; sometimes it was rejected in that state (p. 204). In such cases nothing remained but to work it into the pitch or employ it as fuel, mixed with coals.

Recently the formerly very scanty applications of naphthalene in the manufacture of artificial colours have been considerably increased. To Manchester yellow (= dinitronaphthol) and naphthalene red (magdala red) have been added phthalic acid, as a starting-point for eosin &c. and the long series of azo-compounds. For most of these colours the naphthols, $C_{10}H_7(OH)$, especially β naphthols, are required, for the preparation of which very pure naphthalene, not discolouring in the air, is demanded; and hence such is made by some of the larger tar-distillers.

Naphthalene has also for some time past been used for carburetting gas, *e.g.* by Bowditch †; this employment seems also to be on the increase. Recently a gas-carburetting apparatus, called the albo-carbon light, has been attracting much attention. It is especially adapted for small flames, and saves more than half of the gas consumed for the same illuminating-power in the best argand burners; so that it is very economical, in spite of the cost of the naphthalene. The apparatus should not be allowed to get too hot, lest the naphthalene begin to boil and the apparatus burst.

According to measurements made at Zurich, the following results were obtained:—

* Watson Smith found that the tar made in 1873 and 1874 by the Manchester Corporation gas-works was almost free from naphthalene. In cannel-coal tar he found it along with paraffin. The statement of Crace Calvert, that Newcastle tar contains 58 per cent. of naphthalene, is simply absurd.

† Patent, No. 2937, Oct. 31, 1862.

	Consumption of gas per hour. litres.	Illuminating- power in standard candles.	Hourly con- sumption of naphthalene. grams.
Flüßheim's regulator burner .	111	10·9	—
„ „ .	153	14·2	—
Faas's hollow burner.....	91	9·7	—
„ „	147	17	—
Argand burner	125	10·2	—
„	150	13·6	—
„	167	17·2	—
Albo-carbon lamp No. 1	70	22·5	3-5
„ „ No. 2	95	22	5-7

Fig. 47.



In experiments made by Mr. John Pattinson*, 1000 cubic feet

* Trans. Newcastle Chem. Soc. 1882, vol. v. p. 135.

of gas, along with 4.63 lb. of naphthalene consumed in the "albo-carbon" lamp, yielded as much light as 2700 cubic feet of gas burnt in fairly good flat-flame burners or 1780 cubic feet of gas in argand burners of good construction.

Fig. 47 shows the most usual shape of the albo-carbon lamp. The copper ball *a* is fixed on the socket *c* by means of a stem, *b*, the joint being made merely by true boring-out of *c* and turning *b*; *a* is closed by a screw-cap, *d*, which serves for charging the naphthalene. The gas enters the ball through *c*, *b*, and *e*, and the burner *i* through *f*, *g*, *h*.

Above *i* is fixed the copper disk *k*, which is seen from above in fig. 48. It will be noticed that by moving the slide *ll*, which revolves about a pivot in the centre, the disk *k*, cut out to correspond with *ll*, is either closed or opened.

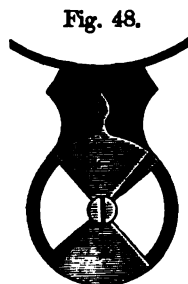


Fig. 48.

The burning gas from *i* heats *k*, which transfers its heat to *a* and heats the naphthalene contained therein a little above its melting-point, say to 80° or 90°. In consequence of this the gas passing through *a* is charged with naphthalene vapour, which greatly increases its illuminating-power. If too much vapour is carried along and the flame begins to smoke, the slide *ll* is moved as in fig. 48, whereby the heating of *a* is greatly diminished.

Phillips's Carbo-Oxygen Gas * means the combustion of naphthalene, dissolved in petroleum, in a current of oxygen. A lamp suitable for this purpose has been described by Carl †; but this process seems to be too troublesome and expensive.

Naphthalene is sometimes employed for *keeping out vermin*, *e. g.* in stuffing animal-skins; Pelouze ‡ recommends it for disinfecting-purposes generally.

* Wagner's Jahresb. 1870, p. 728.

† Wagner's Jahresb. 1872, p. 856.

‡ Bull. Soc. Chim. 1866, p. 351; 1868, p. 258.

CHAPTER IX.

LIGHT OIL AND FIRST RUNNINGS.

We understand by "light oil" that fraction of the first distillation of coal-tar which is midway between the first runnings and the carbolic oil. Some distillers term it "first light oils" or "crude naphtha." At some works, especially on the Continent, no such fraction is made, but every thing coming before the "middle oil," *i.e.* up to 170° , is collected in one receiver. The whole of this must then be subjected to the same treatment as will now be described for the "light oil" as defined above.

This oil contains a little benzene, more toluene, and much more of the higher homologues, together with phenols, naphthalene, and the unknown liquid oils occurring in heavy oil.

Light oil in this sense, if collected up to the point at which the distillate sinks in water, has the following properties. Its specific gravity is about 0.975; it begins to boil at 95° (the bulb of the thermometer dipping in the liquid); but only a little passes over before 120° is reached, from which point up to 171° about 30 per cent. distills. All that distils above this belongs to carbolic oil. But in order to form a correct judgment of the quality of light oil, the distillate up to 171° must be rectified. Thus a sample of not very superior light oil yielded in the first distillation

Boiling-point.	110° .	120° .	130° .	140° .	160° .	171° .
95°	1	3	$4\frac{1}{2}$	9	16	$26\frac{1}{2}$ per cent.,

and on rectifying the $26\frac{1}{2}$ per cent.

Boiling-point.	93° .	100° .	110° .	120° .	130° .	138° .
90°	1	2	5	9	13	16 per cent.

The light oil of trade is of course the more valuable the more easily volatile matters it contains, supposing it to be unadulterated coal-tar oil. Home-made light oil ought to give a good yield up to 171° , but little below 120° : the former proves that the receiver had not been changed too late for carbolic or heavy oil; the latter, that no first runnings have entered into the light oil.

A good deal of light oil is *employed as such*, without purification—*e.g.* for illumination in excavations (where the smoke is of no consequence), for thinning down heavy oil or liquefying pitch to make “prepared tar,” and especially for preparing varnishes for wood and iron (p. 152 *et seq.*). Thenius* makes from it “varnish-oil” by treating it several times with potassium bichromate, manganese, and sulphuric acid, then with water, at last with caustic-soda liquor, and subsequently distilling. Thus a limpid oil of sp. gr. 0.880 is obtained, which does not turn yellow in the air and is an excellent solvent for resins like sandarac, mastic, or copal; so that superior varnishes for photographers and printers, cart-grease, lubricating-oil, &c. can be prepared with it, for which special prescriptions are given.

Most of the light oil is *rectified*, at first by direct fire; only at smaller works is steam used for this product. Along with this oil, either mixed with it or exactly in the same way, is worked up the oil obtained on treating the carbolic oil with caustic-soda solution, after removing the latter (p. 217).

The object of this first rectification cannot be exactly the preparation of commercial products; for this the composition of light oil is still too complicated. For similar reasons it generally does not pay to wash it chemically, except when it has been purposely collected up to the point at which it contains much carbolic acid; and frequently even then its last portions only are treated with alkali. Hence the usual object of rectifying it is, on the one hand, to obtain the most volatile oils (which belong to the same class as the “first runnings” and are treated along with these), and, on the other hand, to separate the heaviest oils which promise no further yield of benzol and go better to creosote or carbolic oil. Between these two a fraction necessarily remains which exhibits some of the characteristics of either. This is always put back into the still and distilled with light oil; so that the latter is ultimately completely split up into the two products mentioned

* Verwerthung des Steinkohlentheers, p. 62.

above, although in each single operation three products are obtained, which we call light-oil naphtha, secondary light oil, and residue. This leads almost universally to making two fractions in the distillation of light oil, and running the third product, as residue, directly out of the still. The question can only be, where to set the limits. Evidently, if the residue is to go to creosote oil, the distillation must be continued till no appreciable quantity of light oil remains behind; and this indicates the limit between the second and third fractions. Where the residue goes to carbolic oil, not even the above is of consequence, since the alkaline treatment in any case separates the hydrocarbons contained in it. In the former case the usual test is, to work till the distillate begins to sink in water; in the latter case the thermometer is usually consulted (see below).

It may be more uncertain where to set the limit between the first and second fractions. Evidently this does not matter very much, since the second fraction is always redistilled. Some English tar-distillers go by the hydrometer, and change the receiver when the distillate shows 10 degrees "under proof" (*i. e.* sp. gr. 0.932), at which point about one fourth part of the light oil has distilled. The second fraction is collected till it begins to sink in water, which corresponds to another 25 per cent., sometimes to 50 per cent. of the light oil.

The first fraction ("light-oil naphtha" or "twice-run naphtha") from light oil obtained in the first distillation of tar shows, for example:—

	Boiling-point.	Per cent. distilling at								
		93°	100°	110°	120°	130°	138°	149°	160°	171°
1.	92°	...	$\frac{1}{5}$	2 $\frac{1}{2}$	9	20	33	50	64	78
1a.	84	2 $\frac{1}{2}$	5	12	24 $\frac{1}{2}$	33	39
2.	107	1	5	17	29	47	64	79
3.	104	$\frac{1}{2}$	3	10	21	44	63 $\frac{1}{2}$	78
3a.	98	...	4
4.	101	4	19	38	52	68	79	90
5.	107	1	5	17	29	47	64	79

1a. is the result of rectifying the first 50 per cent. of 1; 3a, that of rectifying the first 50 per cent. of 3. According to this,

there are great divergencies in the intermediate products; but finally, in all cases, nearly 80 per cent. has come over at 171°. The distillations 1a and 3a show that from light oil toluene, xylene, &c. can be obtained, but no considerable quantity of benzene.

The oils taken off from sodium phenate naturally show rather higher boiling-points, as proved by the following example, where 1 means the distillation of the oil itself, 2 the rectification of the first 41 per cent.

	Boiling-point.	Per cent. distilling at								
		93°	100°	110°	120°	130°	138°	149°	160°	171°
1.	118°	6½	21	41	58	72
2.	5	15	25	32½			

Stohmann-Kerl's 'Chemie' (vi. p. 1175) quotes the following statements from South-German (1) and North-German (2, 3) works :—

	Per cent. distilling at				
	100°	130°	140°	180°	200°
1.	10.6	25.0	...	38.9	57.2
2.	15.4	...	22.5	44.0	
3.	20.3	...	27.12	50.0	

No doubt the "light oil" in this case comprised both first runnings and our light oil together.

Already from these laboratory tests it is evident that the distillation of light oil is best guided by the thermometer. The first fraction might be made up to 170° and worked along with the first runnings from the tar; the second fraction is made at 205° or 210°, the product reworked, and the residue run to carbolic oil. According to Wurtz * the fraction of coal-tar distilling between 150°

* Dictionnaire de Chimie, i. p. 1633.

and 200° (roughly corresponding to our light oil) is worked up thus :—

First Rectification.

a, fraction up to 120°, goes to the corresponding fraction of the principal distillate, received up to 150°.

b, fraction between 120° and 190°, is washed with acid and alkali, then rectified.

c, residue (above 190°), goes to creosote oil.

Second Rectification (of the fraction *b*).

a, product up to 120°, contains benzene and toluene, goes to the corresponding products from the first runnings.

b, product from 120° to 127°, yields solvent naphtha No. I.

c, " " 127° to 140°, " " " " II.

d, " " 140° to 150°, " " " " III.

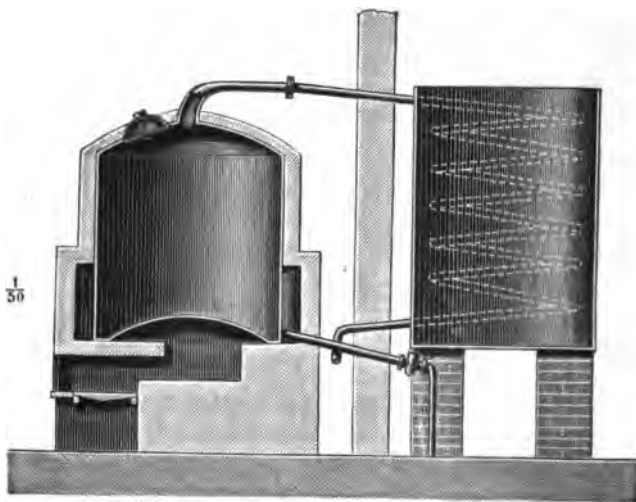
e, residue, goes to creosote oil.

The products distilling from light oil at 170–210°, and above called "secondary light oil," is sometimes employed for washing anthracene (p. 172); or it is chemically washed and rectified, so as to yield solvent naphtha.

The rectification of light oil takes place in wrought-iron stills, usually constructed and set exactly like tar-stills. Only at the largest works are they made as large as the tar-stills; at others a much smaller size suffices, as only a small percentage of the tar passes through them. *E. g.* a still 5 feet wide and 6 feet high suffices for four tar-stills of twice the height and width. It is preferable not to go below the size just mentioned, even at smaller works, but rather to work the still less frequently, or employ it at the same time for the first rectification of the crude benzol. The reason for this is that such a still, holding about 750 gallons, can be easily worked off in a working-day, say 7 to 9 hours, and allowed to stand over night, to cool down the residue before running it out. The still-top is covered with brickwork or some non-conducting material. The still-head is made of cast-iron, and is connected with a 2-inch lead worm, ending in a 1½-inch lead worm, of which the lower part may be only 1 inch wide. A condensing-tub 4 feet wide and 6 feet high suffices for such a still. It should be separated by a wall from the still, as well as the two receivers for naphtha and secondary light oil; the discharge-cock

best passes through the wall as well, so that all these parts are away from the fire, and can be seen at a glance. Fig. 49 shows this arrangement.

Fig. 49.



The discharge-pipe for the residue can be provided with a screw-thread, in order to connect it directly by means of a pipe with the tank for carbolic or creosote oil. This is suitable, because the residue is very hot, even after standing overnight, and gives out very acrid and disagreeable vapours.

Of course the usual mountings must be provided, as man-hole, feed-pipe, air-vent, thermometer; a simple safety-valve (p. 240) is also advisable.

When *working a light-oil still*, a brisk fire is made at first; but this is moderated as soon as the distillation begins, and can be raised again later on. Here, too, some water comes at first, but ceases again after a short time. As long as naphtha comes over, say up to 150° or 170° , cold water must be run through the condensing-tub; but after this the water in the latter and the distillate must be allowed to get warm, because very much naphthalene comes along, and might choke up the worm if it solidified. We have seen (p. 236) that it is still more necessary to prevent this when distilling the oil taken away from sodium phenate. Special care should be taken to arrange the end of the worm so

that the distillate can run out completely ; otherwise, at the end of the operation a plug of naphthalene will be formed there, which might be overlooked in starting a new operation, and might lead to awkward consequences, especially in the absence of a safety-valve. It even happens, if the still is cooled down too much before discharging, that the residue solidifies entirely and cannot be run out without warming the still again.

Some manufacturers prefer heating the light-oil still by indirect steam ; but this does not seem to offer any advantage. It is useful, however, already at this stage to substitute for an ordinary still-head a dephlegmating column, so as to effect a better separation of the product, as we shall see in the next chapter. This is especially advisable when first runnings and light oil are rectified together.

FIRST RUNNINGS.

This term is applied to the first and lightest distillate from the tar-still, as described on p. 113 ; and we shall now show how it is worked up. This fraction is sometimes called first light oils, or once-run naphtha, or crude naphtha, &c. Where no such fraction is made, but the light oil is collected all together, it is nearly always redistilled over a direct fire ; and the "twice-run naphtha" or "light-oil naphtha" thus obtained is treated essentially as we shall describe for our first runnings.

This product contains of course the most volatile constituents of coal-tar, as enumerated in the second Chapter ; but along with them, owing to the peculiar nature of fractional distillation, there are considerable quantities of less volatile bodies. Hence we find in it not merely benzene and its homologues, but sensible quantities of phenols, naphthalene, aniline and other bases, empyreumatic resins, &c. Some of the most volatile bodies are impurities to be removed as completely as possible, as methane homologues, olefines, carbon bisulphide, mercaptanes, nitriles. The "eupion" sometimes mentioned, and Mansfield's allioli, will have to be sought among the latter class of bodies.

Since a distinction or separation of all these bodies is not to be thought of, least of all for technical purposes, it is usual to estimate the quality of first runnings by fractional distillation exactly in the same way as described above (p. 247) for light oil, rectifying again the more volatile portion. The following table shows some of the results thus obtained, in percentages by volume :—

No.	Boiling-point.	88°	93°	100°	110°	120°	130°	138°	149°	160°	171°	Sp. gr.
1.	79°	1	2½	4½	12½	22½	31	37	45	52	62	0·906
2.	84	1	...	15	30	43	51	57	63	69	77	
3.	98	2	...	27	43	54	63	73	83	0·905
3a.	3	15								
4.	91	...	3	10	26	38	49	55	63	71	78	0·908
5.	89	...	½	5	34	45	55	61	68	73	78½	0·911
5a.	9	27½	40	47½						

In all these tests the thermometer-bulb at the beginning of the distillation was just immersed in the liquid; the "boiling-point" hence is much higher than the temperature at which the vapours actually passed over; and even the later temperatures are no doubt too high.

3 *a* is the result of rectifying the first 45 per cent. of 3; 5 *a*, that of the first 61 per cent. of 5.

The table shows that the composition of first runnings varies very much, especially at the lower temperatures, without being indicated by the specific gravity. In fact the latter is quite worthless for the estimation of the commercial value of crude naphtha. A single distillation of the latter does not suffice; and in any case that which has passed over up to 130° should be rectified. Even then the results differ very much if, as is usual in England, the thermometer-bulb is immersed in the liquid, according to the size of the retort, the quantity of the liquid, &c. The only reliable plan is, to place the mercury-bulb at the height of the vapour-delivery tube; and it is even preferable to work with a proper fractionating-flask connected with a Liebig's cooler (fig. 50); best of all with a dephlegmating head, such as Linnemann's three-bulb apparatus, (compare next chapter).

Good first runnings in the first distillation ought to yield at least 10 per cent. by volume up to 100°; in rectifying the product distilled up to 130°, at least 25 per cent. ought to come over up to 100°. Up to 171°, on an average 78 per cent. comes over.

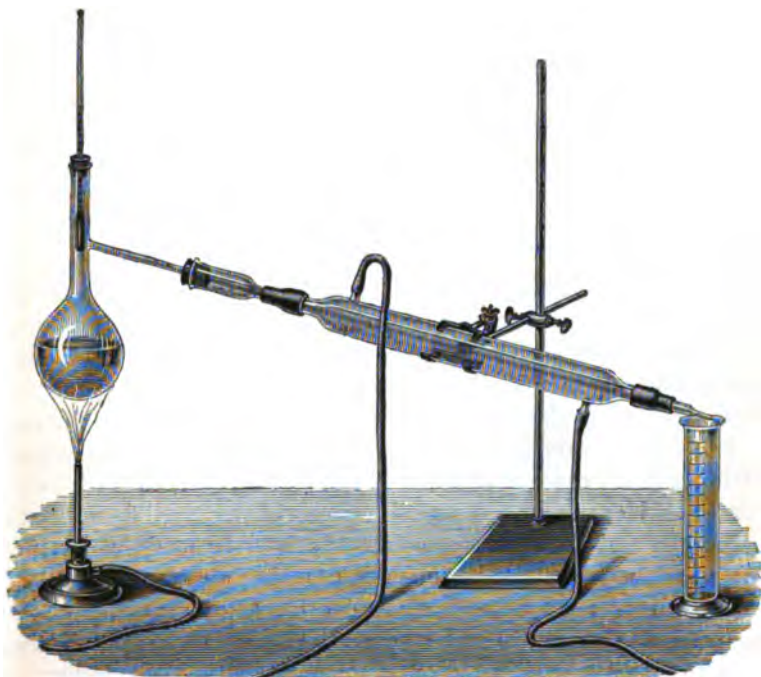
Watson Smith found the following results of first runnings from Wigan cannel-coal tar (p. 140):—

Below	130°	130-140°	140-150°	150-160°	160-170°	170-180°	180-190°
Per cent.	15	20	10	6	9	7	11

The first runnings, as well as the light-oil naphtha, which is

quite analogous to it (compare p. 247) is nearly always *chemically washed* before any rectification, *i. e.* treated with strong sulphuric acid and alkali, less frequently with oxidizing agents. The *functions of sulphuric acid* are :—combining with the bases ; destroying empyreumatic resins ; dissolving olefines ; generally, removing any bodies upon which it acts. Also naphthalene and phenols

Fig. 50.



are converted into sulphonic acids, remaining dissolved in the acid. Its action upon the valuable bodies, *viz.* benzene and its homologues, is very insignificant in the cold if the quantity of the acid is moderate ; but since its action in this respect is not=0, it ought not to be prolonged beyond necessity, and no excess over and above the quantity required for purification ought to be employed. Employed in excess, sulphuric acid forms "sulpho-oils," *i. e.* partly sulphonic acids, partly sulphones, *e. g.* $(C_6H_5)_2SO_2$, which remain dissolved in the hydrocarbons and are afterwards very troublesome, especially in burning.

Only the strongest sulphuric acid of trade, the so-called rectified oil of vitriol, of 170° Tw., can be employed; weaker acid dissolves the bases, but does not act upon the other bodies.

The application of *alkali* (practically always caustic soda) in the case of first runnings, although indispensable, is very much less important than in the purification of petroleum, paraffin oil, or the heavier coal-tar oils, just because the former contain much less phenols, the removal of which is the principal object of this treatment. Hence most manufacturers commence the washing with sulphuric acid, and end with weak caustic-soda liquor. The latter cannot be dispensed with entirely, as it must remove the remaining phenol and every remnant of sulphuric acid and sulphonc acids. In some cases it pays to commence with the alkaline treatment, so as to recover the phenols—especially when first runnings and light oil have not been separated, but are washed together before rectifying. According to Watson Smith, phenol made from first runnings alone has a very disagreeable smell.

The mixing-apparatus for the chemical treatment of crude naphtha must of course be proof against the action of acids and alkalies. Usually it is made of wood lined with lead, the sheets of lead being burned together by the hydrogen-blowpipe. But at some places cast-iron vessels are preferred, which are not so frequently needing repair as lead ones. Cast iron is but little acted upon by the strong vitriol, and is even less so when the latter is charged with tarry matters. Hence cast-iron machinery can be employed for agitation (mixing); and the discharge-cocks may even be made of brass or gun-metal, which would be impossible in the case of pure acid.

The mixers must be well covered over, to prevent the benzol from volatilizing during the operation. In the case of hand work this cannot be carried out so completely as with mechanical stirring, where the shaft passes through a stuffing-box and special pipes are provided for the running-in of naphtha, acid, water, and alkali.

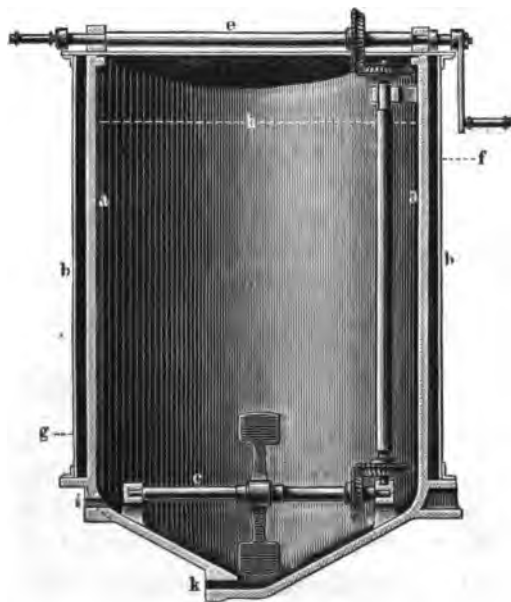
The discharge-cocks must be always so arranged that the dirty acid, as well as the water, can be run out to the last drop. For this purpose the bottom is made to slope to one side, and the cock is fixed in the lowest part in such a way that no portion of it projects upwards; so that any mixture of the liquids in running out can be entirely avoided with some little care.

At small works the mixing of the naphtha with the chemicals

or the water can be done sufficiently by hand, especially as only a small percentage of the tar is subjected to it. This is done with wooden rakes, the head of which is about 15×6 inches and is perforated with six or eight one-inch holes; with these the attendant constantly fetches the acid &c. up from the bottom, which mixes it much better than mere stirring. This should be continued for an hour, or for half an hour at least. In this case the mixer may be circular or square, whilst for mechanical mixing it should be circular. It should be only three quarters filled with the naphtha to be washed.

Evidently mixing by hand is very inferior to *mechanical mixing*, which is, indeed, preferred at all larger works. Sometimes it is done by a finely divided current of air (as described, p. 215, for carbolic oil); but most manufacturers prefer agitating by machinery, because the current of air might carry away some benzene. This cannot be very much, as the mixing need not last

Fig. 51.



above 10 or 15 minutes. We shall mention only some of the most usual mixing-machines. We have already (p. 215) spoken of Hübner's machine, constructed like a churn, in which the mixing

is effected by a perforated piston moving up and down, similar in principle to the mixing by hand with perforated rakes just described. A similar principle was employed in Jung and Must's apparatus *, but with the difference that the motion was not communicated by gearing, but by a steam-cylinder placed directly on the mixer, the piston being attached to the same rod as the mixing-disk. Rolle's mixing-machine † consists of a sloping cast-iron cylinder, whose centre of gravity is situated in the agitating-shaft, provided with scoops for catching the acid and alkali, which, owing to their higher specific gravity, move at the periphery. This machine, as well as that constructed by Vogt ‡, seems less adapted for our purpose than either Hübner's or Jacobi's §. In the latter (fig. 51) the cast-iron cylinder, *aa*, is surrounded by a wrought-iron steam-jacket, *bb* (which can be dispensed with for naphtha, but is indispensable for carbolic acid, naphthalene, &c.), and has a conically shaped bottom. In this tapering part revolve the blades of a horizontal shaft, *c*, which is moved by a lateral vertical shaft, *d*, so that the contents of the mixer are quite accessible. In the arrangement shown in the diagram no stuffing boxes are employed, because the packing could not be made to stand the action of acids, and the latter soon corroded the journals so that no tight joint could be effected. Lining with lead, or asbestos packing did not prevent this. The steam for heating enters at *f*; and the condensation-water issues at *g*; *h* shows the level of the liquid; *i* and *k* serve for discharging the oil and the washing-agents. The vessel *aa* should be cast in one piece, and with the bottom turned downwards, in order to avoid flaws, which would be very injurious in presence of the acid. The shaft *e* revolves 45 or 50 times, the agitating-shaft *c* 64 or 72 times per minute. This apparatus, which holds 3 tons, can be set in motion by two men, without any steam power, as the mixing only lasts a few minutes at a time.

The mixer should be placed at a sufficient elevation to run both the acids and other liquids into suitable places. The dirty acid is sometimes emptied into carboys, but is usually carried away to an outside tank, by a lead spout.

* Described by Fuhst, Dingler's Journal, clxvi. p. 21.

† Wagner's Jahresb. 1862, p. 680.

‡ Dingler's Journal, clxvii. p. 261; Jacobi (ibid. clxviii. p. 264) declares it to be quite useless.

§ Dingler's Journal, clxviii. p. 261.

The washing-water is not run straight away, as it is next to impossible always to prevent a little oil from coming along with it. This oil can be saved by the drain commencing in the mixing-house itself with a catch-pool, in which the washings are first collected. The floor is made to slope from all sides towards this catch-pool, so that any oil spilt anywhere can be washed into the pool. The liquid does not run into the drain from the top of the catch-pool, but through a pipe reaching nearly to its bottom, bent at an angle at the top and passing through the side of the catch-pool into the drain. Since thus the drainage takes place from the bottom of the catch-pool, the oil remains quietly at the top, and is taken off from time to time.

The *operation of mixing* is performed in this manner:—When the naphtha has been pumped into the mixer, it is first allowed to rest quietly for some time; and the never-failing water, which collects below, is *completely* drawn off before adding the oil of vitriol, which would otherwise be diluted. A careful workman can, both in this case and in all analogous ones, run off the water without a drop of oil, by cautiously regulating the tap, observing the colour, and touching the liquid with his finger. If any oil should run off through some mishap, it is retained in the catch-pool.

The quantity of acid must vary according to circumstances, but not so much as might be imagined. A little above 1 lb. of oil of vitriol per gallon of oil suffices both for first runnings and light-oil naphtha (p. 247). If more is added, there is more loss of oils; if less, the distillates, especially the burning-naphtha, are discoloured by standing and contain naphthalene. Freshly distilled oils take less acid than old ones, in which more “empyreumatic resins” are found. The above proportion is equal to 12 parts oil of vitriol to 100 parts naphtha by weight.

With a mixing-machine, 10 or 15 minutes suffice for thoroughly working up acid and oil. After this at least an hour must elapse to allow the liquid to settle. It is best to mix at the end of the shift, and to let the liquid settle overnight, but not any longer, because otherwise the dirty acid turns so thick that it will not easily run out; sometimes great lumps of a pitch-like substance are found, which choke up the tap. If the acid is too thick even after shorter settling, this is a proof that very many impurities

were present—*e. g.* tar which frothed over into the first runnings, or light oil from the light-oil still. In such a case more acid will have been required, and more alkali will have to be used afterwards. Thus even previous mistakes of the men can be discovered afterwards. On the other hand, if the dirty acid is too thin, this is a sign that too much acid has been used, or that the water had not been completely run off previously. Neither of these ought to occur. Generally the acid will be found to have doubled its bulk by taking up tarry matters.

The acid must be run out to the last drop; and the bottom of the mixer must be constructed accordingly (p. 254); for any remainder of acid, on being diluted with the washing-water, separates again a large portion of the dissolved bodies and thus contaminates the naphtha over again, certainly more mechanically than by solution, as the tarry matters, when changed by sulphuric acid, are hardly soluble in naphtha. For this reason alone the *dirty acid* or *waste acid* (sometimes called *vitriol-tar*) must never be run off through the catch-pool and common drain (p. 257), which would be stopped up directly; it must be run by an open shoot into the main sewer, or, if it is feasible, directly into the river, or else into a special tank, or into carboys, casks, &c. Wooden casks last some time, as the corrosive action of the acid is greatly weakened by its tarry admixtures; but they are acted upon in time.

The specific gravity of the dirty acid is about 1.365; and it contains as much acid as corresponds to 45-per-cent. rectified oil of vitriol. It is for the tar-distiller the most troublesome waste product imaginable, killing, as it does, all fish in canals, brooks, and rivers, and perceived at great distances by its stench and the red colour of the water. Of course distillers have incessantly tried to work it up in some way, even without any profit. That this is no easy matter seems proved by the fact that in *none* of the tar-works visited by the author had any use been found for this acid, and that it was everywhere allowed to run away or sink into the ground somehow. In any case it ought first to be neutralized with lime.

If such tar-acid is diluted with its own bulk of water, most of the impurities rise to the surface as a tough, tarry substance of most disagreeable smell, and can be skimmed off. This matter, evidently containing derivatives of fatty hydrocarbons, does not

occupy much bulk and can be got rid of by a hole in the ground, or, wherever the sulphurous acid is of no consequence, by burning. Perhaps a useful colouring-matter might be prepared from it; for in alcohol it dissolves with a fine red colour. It is insoluble in benzene or naphtha.

The remaining acid is still red and disagreeably smelling, as it still retains a little of the tarry substance. It might be employed for neutralizing ammonia, for making sulphate of iron or copper, &c.; but even this is difficult, as the products are affected by the impurities of the acid. If used for making superphosphate, the tarry substances might protect the roots against insects, &c.; and this use of it seems to be actually the rule in Scotland. We have seen (p. 219) that it cannot be employed for saturating the sodium phenate; for, besides the colouring-matters, the sulphonic acids would spoil the phenol.

At Young's paraffin-works near Edinburgh the vitriol-tar was formerly evaporated to dryness, and the residue burnt. By this the sulphuric acid was converted into sulphur dioxide, which could be utilized in vitriol-chambers. In the great majority of cases no vitriol-chambers are at hand; but the vitriol-tar might still, without dilution, best, perhaps, mixing it with sawdust, be converted into sulphur dioxide by heating in iron vessels, and that compound be utilized for preparing sulphites or hyposulphites.

A patent taken out by W. P. Jenny in Germany (No. 3577) refers to the vitriol-tar from the washing of petroleum; but if it is at all useful, it must also apply to our case. According to one method the acid is to be diluted with its own bulk of water; the tarry oil precipitated is to be washed several times with boiling water, and at last with a little soda. It is then distilled up to 250° and the residue in the retort treated for 48 hours with a current of air. The oxygen is absorbed with avidity; and a mass is formed which, after cooling, is a dark-brown resin. According to the other method the dirty acid is heated to 100° or 150° for several days, till a sample sinks down in water. It is then poured into water; and the precipitated substance is washed with much water; or else its own bulk of petroleum spirit is first added, in which case the mixture floats at the top. The product is more or less hard, according to its degree of oxidation, and is insoluble in water, alcohol, and alkalies, but soluble in all fats and oils,

naphtha, benzene, &c., as well as in the strongest sulphuric acid. Melted up with india-rubber or gutta percha in different proportions, it forms an elastic body which can be used as an insulator; dissolved in light petroleum spirit, it yields a serviceable asphalt varnish.

To return to the washing of naphtha—when the acid has been drawn off, *washing with water* follows. Water, amounting to about one fifth of the bulk of the naphtha is run in, mixed up with it for a quarter of an hour, and allowed to settle for half an hour. The water, which has now acquired a deep red colour, is run off by the bottom tap, every precaution being taken against oil coming along with it, and flows away through the catch-pool sunk in the floor of the house (p. 257). This operation is repeated three or four times, and, if the fourth water is still coloured, even a fifth time. Even the fifth water tastes rather bitter, perhaps from naphtha; it may also react very faintly upon litmus; but it ought in no case to show any colour.

Now comes the *alkaline treatment*. The caustic-soda solution may be dilute, sp. gr. about 1.100. Its quantity cannot, like that of the acid, be fixed beforehand, but differs in each operation between $1\frac{1}{2}$ and 6 volumes of that dilute solution for 100 volumes of tar-oil. The liquor is gradually added during the agitation, until a change of colour has taken place in the tar-oil, when nothing further is added. Usually the colour changes from reddish brown to light brown or brownish yellow, and that very abruptly; but sometimes blue or purple colours are observed. Finally the liquids are well mixed up, and then left for an hour to settle; the caustic liquor is drawn off from the bottom; the naphtha is twice washed with water, and is now ready for distillation. In Lancashire milk of lime is used instead of caustic soda.

The *loss in chemical washing* amounts on an average to 8 per cent. by volume of a mixture of first runnings and light-oil naphtha. Good oils lose only 5, or even 4 per cent., bad ones as much as 12 per cent. Fresh products require less chemicals than old ones, and lose less by the treatment. Careless working, where much naphtha runs away with the water, may double or even more than double the loss; and even the catch-pool does not quite prevent this, as some of the naphtha remains suspended in the water.

When testing purified naphtha by distillation, the boiling-points are usually found rather higher than those of the unwashed naph-

tha. This proves that the removal of less volatile bodies (phenols, naphthalene, bases) is more than compensated by that of more volatile ones (methanes, olefines, sulphur compounds). Complete purification, so that nothing but benzene and its homologues remain, cannot be expected; carbon bisulphide especially remains, often in very appreciable quantities.

The mixing-apparatus is best fixed in the same room as the steam-stills with their receivers and the receivers of the benzol-still (see below). Considering the great danger of fire, this building ought to be constructed without any wood, with an iron roof (for instance, one of corrugated sheet-iron). The roof should be provided with movable ventilators. Open fire (even matches) ought never to be tolerated in this room; it ought to be lighted by reflectors from without, or by electricity. Inside and outside hydrants and hose ought to be provided, so that every place may be reached by a jet of water. It has been observed * that pure water is not very suitable for putting out fires of light tar-oils, because these float on the top; but ammonia-water, which is always at hand, does excellent service in this way, probably owing to the volatilization of ammonium carbonate and sulphide; and putting on sand, ashes, and the like acts better than water. The safest plan would be to have one or more pipes leading from the steam-boiler into the room, through which it could be filled with steam by taps or valves *accessible from the outside*; thus the air would be driven out and the fire quenched.

The washing process described above is probably that generally employed, except in the case mentioned on p. 254, when an alkaline treatment is interposed before the acid, in order to get the phenols. The employment of the other processes, now to be mentioned, seems to have been discontinued.

Mansfield used, for every gallon of benzol, $\frac{1}{4}$ lb. of sulphuric acid and one ounce of nitric acid of spec. grav. 1.30, sometimes also a little bleaching-powder and hydrochloric acid. For toluene he took $\frac{1}{4}$ lb. sulphuric and $\frac{1}{4}$ lb. nitric acid. For the alkaline treatment he took lime-water or caustic-soda solution. The less volatile hydrocarbons were boiled for 5 or 6 hours with a quarter of their volume of caustic-soda solution, sp. gr. 1.130, with reflux

* The author noticed this many years ago, also in his German work on tar-distilling (p. 101); Watson Smith (private communication) confirms it.

of the distillate ; the liquid was then distilled and purified by dilute sulphuric, nitric, or hydrochloric acid.

Ronalds and Richardson prescribe twice treating with sulphuric acid, mixing for several hours, whereby much heat is evolved (probably by excessive action), washing with water and ultimately with lime-water or dilute caustic soda. They warn against allowing the light to act upon fresh naphtha, because in that case the water will not readily settle down.

Young * treats with bleaching-powder, adds dilute hydrochloric acid gradually, and at length caustic-soda solution ; the oxidized products collect at the bottom as a black layer, from which the clear oil is easily drawn off. In this way the tar from gas-works in which the richer Scottish cannel coals are used can be advantageously converted into the ordinary products of the paraffin-oil industry (?).

According to Breitenlohner's experiments with peat-tar oils † the employment of oxidizing agents, as well as lime in lieu of caustic soda, leads to so much inconvenience that, after all, sulphuric acid and caustic soda must ultimately be resorted to.

Treatment of the washed Naphtha.

This can take place in various ways. Some distil the product at once by steam, and collect the distillates as benzol, solvent naphtha, &c. ; others interpose a distillation by direct fire and fractionation. The former process seems at first sight shorter and simpler ; but it is advisable only when time presses, since by this plan the last products, especially the burning-naphtha, cannot be kept from discolouring in the course of time. This can be easily prevented by employing the second process, *i. e.* first distilling once more over a direct fire, and making two or three fractions.

This is done in a still exactly like that used for light oil (p. 249) ; for the sake of cleanliness, it is advisable not to employ the light-oil still itself, but a special *crude-benzol still*. Its worm is made of lead, and, on account of the great volatility of benzol, is rather long. The still and its worm are placed under a shed outside the mixing-house ; but the three receivers are either placed inside the

* Hoffmann's Report by the Juries, 1862, p. 140.

† Dingler's Journal, clxvii. p. 378.

house, or at least connected with it by pipes so as to be accessible from within. They consist of well-riveted iron boxes with a man-hole and a small hole for running in the distillate from the worm; the latter hole must just fit the pipe, and must be closed by a plug except when in use. This is done both on account of loss by volatilization and of danger from fire, since benzene vapours, even very much diluted with air, take fire most readily.

In firing, the same principle is followed as usual—strong firing during the heating-up, to be moderated immediately when distillation commences. At first the cooling-water is run as fast as a 1-inch water-pipe will permit, so that the distillate runs off quite cold; only towards the end should it run out tepid.

The fractionation is regulated by the thermometer, which is always fixed in the still. This has the drawback that the attendant must be depended upon for timely changing the receivers. But he can be easily controlled by distilling 100 c. c. from a glass retort with thermometer, and noting the quantities passing over at the desired temperatures; according to very many experiments made by the author, the same result is obtained as on the large scale. The volumes thus found are calculated for the quantity put into the still (as measured by an iron gauge rod in the mixer, or in any other way); and the attendant is instructed to run so many inches depth into each receiver. If there are tables of the contents of each vessel, the whole, including the calculation, can be done in ten minutes. By this plan a thermometer in the still itself can be dispensed with altogether.

The fixed points of the fractionation must vary according to the desired final products. For 90-per-cent. benzol, the first fraction is made at 110° , the second at 140° , the third at 170° , and the still is then stopped. For 50-per-cent. benzol two fractions suffice, up to 140° and from 140° to 170° . The second fraction, as we shall see, yields next to nothing distilling below 100° , and thus serves only for naphtha. It is not advisable to go beyond 170° , as as this would injure the quality of the last naphtha; it is better to allow the still to cool overnight, and to work up the residue eventually, together with light oil, to extract every trace of benzene homologues. The distillation of about 750 gallons lasts 8 or 9 hours, so that a still can be worked off in a winter day; it rarely needs cleaning.

The following table gives some idea of the quantities of the

products obtained, in percentages by volumes of the raw material:—

	Distillate up to 140° (first product).	Distillate from 140° to 170° (second product).	Residue in the still.
First runnings alone	60-61	15-17	20-22
Light-oil naphtha	30-33	40	
Mixture of both.....	48-52	22-26	

CHAPTER X.

RECTIFICATION BY STEAM. FINAL PRODUCTS.

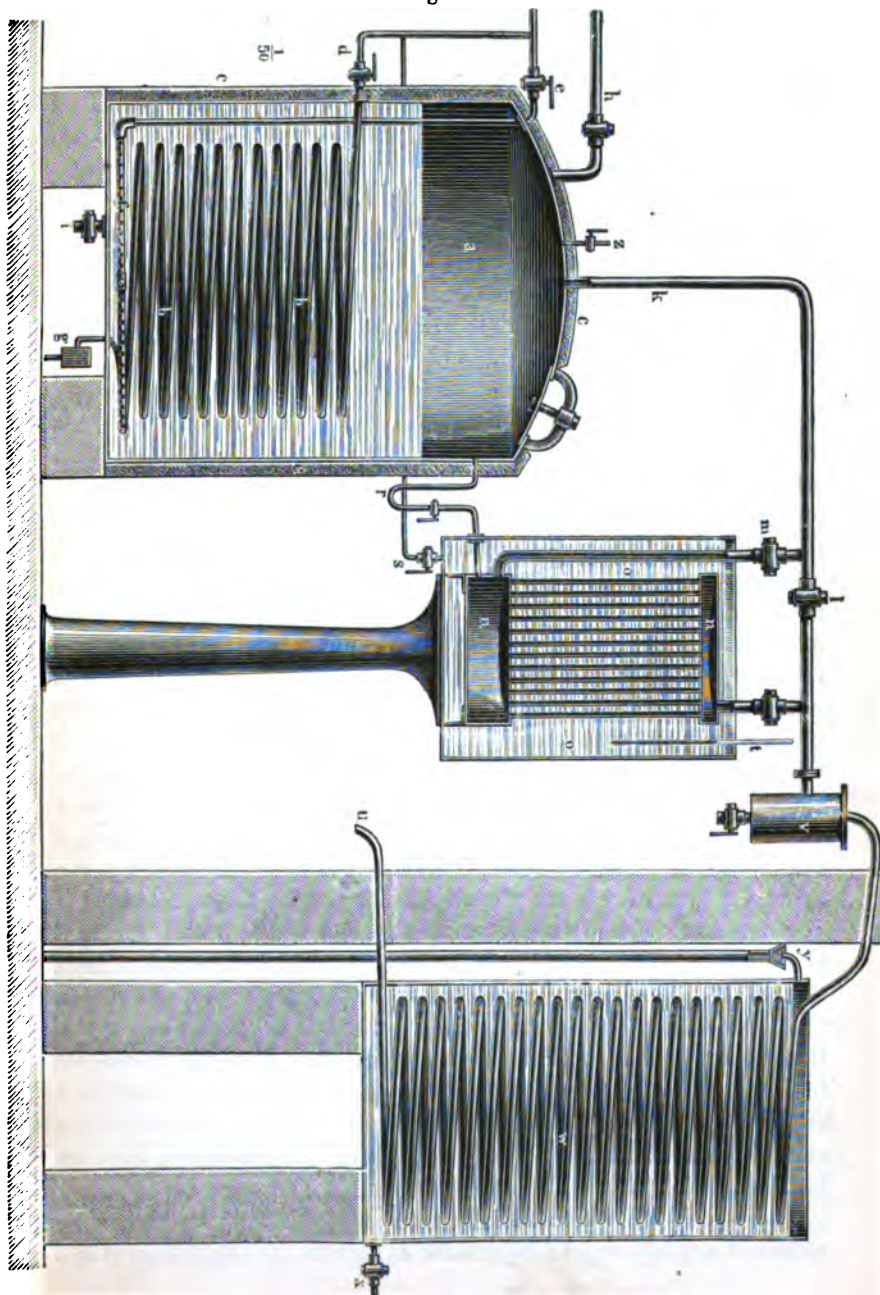
THE last rectification of light coal-tar oils is always effected by means of steam, either indirectly applied (dry steam) or blown directly into the liquid. In the latter case the steam carries away a great deal of substances boiling at a higher temperature than its own (according to the principles explained, p. 115); and it is hence reserved for the last stage, after the indirect steam has exhausted its action. As a rule, the steam-stills are adapted to either. They also always possess some arrangement for partial condensation or dephlegmation, to effect a better separation of the final products.

The steam ought to have a tension of at least $2\frac{1}{2}$ atmospheres, preferably more. It should be, if not exactly superheated, at least completely dried—*e. g.* by passing it through a coil of pipes, or through a long and shallow iron box, surrounded by the waste heat of the boiler-fire.

We shall now first sketch two different systems of steam-stills, whose principal parts might be mutually exchanged, so that the dephlegmator of the second system might be attached to the first still, and so forth.

Fig. 52 shows a system found in operation at large English tar-works. *a* is the still, made of boiler-plate, cylindrical with flat bottom and convex top; *b b* is a wrought-iron jacket round the sides and bottom; *c*, a non-conducting casing of some sort for preventing the loss of heat; *d* and *e* are steam-cocks, *d* supplying the steam-jacket, *e* the perforated coil *f* inside the still; *g* is a self-acting water-ejector for the coil *f*. The pipe *h* serves for feeding the still with crude benzol, *i* for discharging the residue, *k* for

Fig. 53.



carrying away the vapours. The latter pipe communicates by the top *l* directly with the worm, placed outside the still-house, or else, when *l* is shut and *m* is opened, first with the dephlegmator or "condenser" *nn*, made of lead or iron tubes. The latter is placed in the water-filled vessel *o*. The liquid condensing in *nn* collects in *p*, and flows through the vessel *q* and the hydraulic lute *r* back into the still. *q* sends a branch into the main vapour-pipe; but the bends of the pipes prevent the vapours from passing directly from *a* into *q* and thus into the worm. Through the steam-pipe *s* the water in *o* can be heated at will, this being regulated by the thermometer *t*. *u* is the bottom end of the worm, returning into the still-house.

In the second system (fig. 53, the similar or analogous parts being denoted by the same letters as in fig. 52), *a* is the still, indirectly heated by the steam-cock *d*, which communicates with a leaden or wrought-iron coil *b* with water-ejector *g*. Direct steam can be blown in through the cock *e* and the perforated cross of pipes *f*. *h* is the feed-pipe, *i* the delivery cock, *k* the still-head. To carry the vapours away at once, the cock *l* is opened, when they first pass through the box *v* (for retaining any liquid carried over mechanically—a contrivance which should never be absent), and then enter the worm *w*, made of $1\frac{1}{2}$ -inch lead pipe, whose end at *u* returns into the still-house, where also the receivers are placed. The worm-tub is fed with water by *x*; at *y* the hot water runs off. If the vapours are to be dephlegmated, the tap *l* is closed and *m* opened. The vapours then enter the condenser *nn*, whose lower drum communicates with the upper one by fifty copper pipes of $\frac{3}{8}$ -inch bore. The condensed oil returns into the still by the hydraulic lute *r*: *s* is the steam-pipe for *o*, *t* the thermometer.

The second system appears to be superior to the first. Internal heating by a steam-coil is quicker and attended by less loss of heat than heating by a steam-jacket; and the dephlegmator represented in fig. 53 especially acts more thoroughly, and impedes the passage of the vapours less than that shown in fig. 52. Either is preferable to a simple worm, in which the ascending vapours are sometimes stopped by the backflow of condensing oils. Some manufacturers employ proper rectification-columns, as will be described later on in connexion with Savalle's apparatus.

The steam stills are charged with washed naphtha either by means of a pump or an air-pressure apparatus, or else from a store-

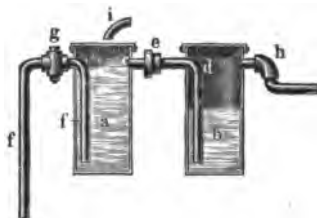
tank placed at an elevation, into which the naphtha has first been pumped. Meanwhile the air-vent (seen at *z* in fig. 53) is opened; it is either a tap or simply a 1-inch aperture, afterwards closed by a cork or a screw plug. Through this hole an iron gauge-rod can be introduced, in order to ascertain the level of the liquid in the still. The man-hole is only opened at longer intervals, for cleaning the still.

It is the rule to pump first the most volatile products into the still, and work them by indirect (dry) steam, then the less volatile products, which are first treated by indirect and afterwards by direct steam. If two products have been made in the benzol-still (p. 262), they are worked separately—viz. the second at once with direct steam, which can be done in a special still fitted merely with an arrangement for blowing-in open steam; the distillation of the first product we shall now describe.

Steam is admitted with full force through the tap *e* into the steam-jacket or the steam-coil *b* (the letters refer to both figs. 52 and 53). As soon as the liquid begins to boil and to distil, the steam-cock is almost closed, and is then regulated so that the distillation goes on continuously but not too quickly, not to say tempestuously; otherwise there would be loss by incomplete condensation, and danger of fire. At first a little water comes over, which often makes the benzol quite turbid; but this need not be minded, as the benzol soon clears up, either in the receiver or in the store-tanks. Later on, when direct steam has to be used, of course very much water appears, which must be separated from the naphtha. This can be done by the apparatus shown in fig. 54, for instance, which at the same time permits the naphtha to be finally purified by dilute caustic-soda solution. Two open cylinders of tin-plate, *a* and *b*, 9 inches wide and 2 feet high, are each provided at the top with a channel, serving as a water-lute, into which a tin cover is put; they are connected by the two pipes *c* and *d*, which can be quickly joined or separated by the screw-cap *e*; *c* ends open 1 inch below the top of *a*; *d* bends down inside *b*, and ends just above its bottom. From the bottom of *a* the pipe *f* rises up, passes out, and leads to a waste-pipe; it can be shut off by *g*. From *b* the pipe *h* takes away any liquid just below the top. *f* and *e* must leave *a* exactly at the same level; *h* may be at the same or at a slightly lower level. At *i* the end of the cooling-worm is sketched.

Before starting, *a* is three quarters filled with water. As soon as the mixture of naphtha and water comes out of *i*, *a* is quickly filled up to the level of *c* and *f*, and its contents run out of these two pipes; but as water and naphtha instantly separate, only naphtha will run away from the top (through *c*), and only water

Fig. 54.



from the bottom (through *f*). If *f* were below *c*, the former would fill entirely and act as a siphon, which should not take place. For use in case of need the tap *g* is provided; but this should never be required.

From *c* the naphtha runs over into *b*, fills this vessel, and runs away into the receivers through *h*. At the last stage, *b* is half filled with dilute caustic-soda solution (sp. gr. 1.100), so that the naphtha must pass through it; why, we shall see later on.

At least *two receivers* are needed; these suffice, if the distillates are run or pumped straight from them into store-tanks. For the receivers, instead of closed iron tanks, open vessels with loose covers are preferable, as these can be easily inspected and cleaned after each operation, so as to ensure that the final products are quite pure and colourless. In this case, since iron would rust quickly and the water would cause a red mud to be formed, wooden boxes lined with zinc or lead are employed, with their bottom sloping a little to one side, and a tap fixed at the lowest point, so as to draw off their contents completely, either into a store-tank or into a pump.

The usual process for separating the distillates is as follows:—First, as above mentioned, only indirect steam is admitted through the tap *e* (fig. 52 or 53). The most volatile products escape first; but from the first, along with benzene, a little toluene also distils,

and later on much more, which is unavoidable in any fractional distillation, as explained, p. 116. But since in trade specific qualities of commercial "benzol" are required, means must be sought for obtaining these as directly as possible, with the least possible quantity of intermediate products to be worked over again. For this purpose the principle of partially condensing the vapours, with reflux of the condensate into the still, is always employed, as was done already by Mansfield; this is the same as has long been known in spirit-distilling as "dephlegmation." It is effected by the condenser *nn*, in the vessel *o*. By closing the tap *l* and opening *m* the vapours arriving by *k* are compelled to enter *nn*, the water in *o* being heated by the steam-pipe *s* to the required temperature. For 90-per-cent. benzol the water-bath should be kept at 60°, for 50-per-cent. benzol at 70°–80°; but these temperatures cannot be absolutely fixed beforehand, and must be found out by experience for each apparatus; in any case they should be kept as constant as possible. The liquor condensing in *nn* returns through *r* into the still *a*; it is essentially toluene, with a little benzene. Some manufacturers allow it to run back into *a* directly and continuously (fig. 53); others interpose a small intermediate vessel (*g*, fig. 52), if the shape of the condensers makes it more advisable to allow the vapours given off in *g* to get into the main delivery-pipe. Others run the condensate from *n* into a separate closed receiver, in order to rectify it separately. The uncondensed vapours of benzene, with a little toluene, now enter the main vapour-delivery-pipe, then the worm *w*; and the benzol condensed therein runs through *u* and the separating-cans, fig. 54, into the receivers.

After some time, nothing further will come out of *u*; and now it is time to raise the temperature in *o*, to obtain weaker benzol. Usually it is possible, even for making pure toluene, to work with water in *o*, heating it to the boiling-point. Water is all the less applicable, if only 30- or 40-per-cent. benzol is to be made, which is the rule. At most tar-works, in the further distillation no separation into pure hydrocarbons is aimed at, and hence the dephlegmation is not carried further. When nothing further runs from the worm *w*, the condenser *n* is put out of work by closing the tap *m* and opening *l*. Now all vapours pass directly into *w* and are condensed, so that again a considerable quantity of distillate is obtained. Gradually this ceases; and when little or nothing comes over, the indirect steam from *e* is stopped and direct steam is in-

jected through *d* and the apertures of *f*. Even with steam of only $2\frac{1}{2}$ or 3 atmospheres an ample quantity of xylene and trimethylbenzene is carried over, which mixture we shall describe afterwards as solvent and burning-naphtha. Xylene is now employed as such in the manufacture of colours, and is for this purpose separated in Savalle's column apparatus (see below).

We must now see on what principles the fractionation takes place. It seems the simplest course to be guided by the thermometer in the still or in the dephlegmator; but as the first requirement is to obtain products fulfilling certain commercial tests, and it is not very easy to carry this out by means of the thermometer alone, other matters must be taken into account. We shall first describe the process carried on at a tar-works possessing a still with rectifying-column, and working chiefly by the thermometer. Distillation by steam is there performed *twice*. In the first distillation the following fractions are made:—

- 1st, up to 103° (thermometer in the still), yields 65–70-per-cent. benzol;
- 2nd, 103 – 110° , yields 30-per-cent. benzol;
- 3rd, 110 – 130° , yields nothing at 100° , 60-per-cent. at 120° ;
- 4th, above 136° , yields solvent naphtha.

In the second distillation the dephlegmator has the principal work to do. By rectifying fraction 1 and keeping the dephlegmator at 56° , 90-per-cent. benzol is obtained; with the dephlegmator at 80° , 50-per-cent. benzol comes out. The thermometer in the still, as long as 90-per-cent. benzol comes, never exceeds 100° . When this temperature is obtained, fraction 2 of the first distillation is run in, and the temperature in the still is allowed to rise to 105° , that of the dephlegmator to 80° ; the receiver is also changed, and 54-per-cent. benzol obtained. Now the receiver is changed again, open steam is injected into the still, and the distillate collected as solvent naphtha. It would be quite possible in the same apparatus to make pure toluene.

Other manufacturers are not guided by the temperature in the still, but only by that of the dephlegmator; and this seems preferable. It is certain that after some experiments with any special apparatus, and carrying on the previous operations on the same plan, the regulation of the temperature of the dephlegmator will by itself permit any desired product to be got; *e. g.* it will be possible to

manage so that the whole distillate, when it is mixed up, shall yield 50-per-cent. benzol. The receiver will then be charged for the first time when nothing further passes through the dephlegmator, for the second time when indirect steam does not yield any thing even after shutting off the dephlegmator, so that a third product is to be obtained by open steam.

None of these marks can be implicitly trusted to furnish products fulfilling distinct commercial requirements. Hence during the operations several laboratory tests must be made; and some manufacturers depend entirely upon these. The testing is done in a glass retort, or, better, in a fractionating-flask with Liebig's condenser (fig. 50, p. 253), taking as fixed points for the fractions only 100° and 120°, and for the later distillates also 130° and 160°.

In most cases a previous laboratory test of the charge in the steam-still will give an approximate idea how much of each fraction may be expected. In accordance with this a sample is taken a short time before it is believed the receiver will have to be changed, after well mixing up its contents. Supposing 90-per-cent. benzol to be aimed at, if the test shows that the contents of the receiver just give 90 per cent. at 100°, of course the receiver must be immediately changed, since it cannot be expected that this strength will remain for any length of time if the distillation be continued. Properly speaking, the distillate ought to be always rather stronger than necessary before being pumped into the store-tanks, to make quite sure of its being sufficiently so. Before being pumped away, its height in the receiver is gauged, and the volume (to be ascertained by a table) and analysis are noted. It must now be brought exactly to the proper strength by adding a calculated quantity of the contents of the next receiver. Supposing this to be found = 70 per cent. benzol, its contents will have to be divided among the store-tanks for 90- and 50-per-cent. benzol. The calculation is made in the following manner:—Supposing 120 gallons of 95-per-cent. benzol to have been pumped from the first receiver, and 160 gallons of 75-per-cent. benzol to be found in the second, the question is, how much of the latter must we pump to the former in order to obtain a commercial product of 90 per cent? We shall learn this from the proportion:—

$$120 \times 95 + x \times 75 = (120 + x) 90;$$

$$120(95-90) = x(90-75);$$

$$x = \frac{120 \times 5}{15} = 40.$$

That is to say, to the 120 gallons of 95 per cent. another 40 gallons of 75 per cent. should be added, to obtain 120 + 40 gallons of 90 per cent. The remaining 120 gallons of 75-per-cent. benzol are pumped into the store-tank for 50-per-cent. benzol, and both quantity and quality noted. Suppose now that the third receiver is found to contain, say, 144 gallons of 40-per-cent. benzol. We shall now put:—

$$120 \times 75 + 144 \times 40 = (120 + 144)x;$$

$$x = \frac{14760}{264} = 55.9.$$

This means, if the whole contents of the third receiver be pumped to the 120 gallons of 75 per cent., the mixture will still be 56-per-cent. benzol, and will bear an addition from the contents of the next receiver. But the examples already given will suffice to show how the calculation is made for this or any similar case. Frequently the benzol in the tanks is kept rather above the standard, and is only brought down just before it is sent out; but care should be taken to do this invariably with the immediately following, not with any later fraction.

If no 90-per-cent. benzol at all is required, all the above-mentioned distillates would be pumped into the tank for 50-per-cent. benzol, always noting both quantity and quality. By multiplying each time the number of gallons by the percentage, and dividing the product by the total number of gallons, the percentage of the mixture will be found. The "percentage" in this case is no doubt only an apparent one; a 50-per-cent. benzol has no analogy with a 50-per-cent. solution of a salt or with 50-per-cent. spirit of wine; but practice has shown that calculations like those exemplified are quite trustworthy. As a rule they make the product appear slightly below its actual strength; but this is a fault of which the buyer will not complain, and which the tar-distiller might easily correct if he cared to do so. In the case of

important contracts, of course such calculations will not be depended upon, but the mixture must be specially tested.

Besides 90- and 50-per-cent. benzol, frequently 40-, or even 30-per-cent. benzol is required in trade. What now comes, is mostly toluene, and is sometimes sold as such. Commercial toluol ought to yield 90 per cent at 120°. But the next fraction after benzol is sometimes destined for *carburetting-naphtha*. According to a specification proposed by Dr. Letheby and adopted by several gas-works, such naphtha ought to yield at least 70 per cent. at 130° and 90 per cent. at 150°; its specific gravity ought to be 0.85–0.87. In practice, only the first point need be taken care of; the others will follow of course. This product essentially consists of xylene. The specific gravity proves the absence of any adulteration with petroleum spirit. When passing from benzol to carburetting-naphtha, half-filling the second separating-can (*b*, fig. 54, p. 270) with weak caustic-soda solution should not be omitted. If there is no sale for this product, it is redistilled and split up into benzol and solvent naphtha.

According to a table given in Wurtz's 'Dictionnaire de Chimie' (i. 1633), French tar-distillers would seem to fractionate in a different manner. The first principal fraction received consists of the tar-oils boiling from 30° to 150°. They are first redistilled in boilers of 2000 litres capacity by open fire or steam; two thirds are distilled off, and the residual third run to the second fraction, viz. the oil boiling between 150° and 200° (compare light oil, p. 248). The above two thirds are treated with acid and alkali, and rectified afterwards, the following fractions being made:—

- a*, boiling from 30–70°, pentane, hexane, &c.
- b*, „ „ 70–110°, benzene and toluene.
- c*, „ „ 110–127°, benzine No. I. for removing grease.
- d*, „ „ 127–140°, „ No. II. „ „
- e*, residue, goes to the second principal fraction.

But it is not possible to separate the hydrocarbons as easily and completely as is indicated in that place. None of the tar-works known to the author proceed in this way.

That which follows the weakest benzol, or the toluol, is received as *solvent naphtha*; and some manufacturers make no further fraction, but put to this also every thing obtainable from the liquid by direct steam. The name is derived from the fact that

this product is used for dissolving india-rubber in the manufacture of waterproof fabrics. Of late it has been extensively employed in the manufacture of anthracene (p. 170) ; and it also serves for removing grease-spots. It consists principally of xylenes and trimethylbenzenes, no doubt also of other bodies not well understood. The india-rubber-manufacturers require the solvent naphtha to be entirely free from naphthalene, which may occur in small quantity in the last distillate by steam. Hence distillation should not be carried too far, but should be interrupted when the product yields 90 per cent. at 150° (some allow 160°) and its specific gravity does not exceed 0.875 at 15° . This will be the case with the whole as soon as a sample of the distillate, as it flows from the worm, shows 0.880 at 15° . Since differences in temperature cause very important differences in the specific gravity, to reduce the observed to the normal temperature (which can be done by means of the table in the appendix) should never be neglected.

If special stipulations are made for the delivery of solvent naphtha, and if on the other hand there is a sale for *burning-naphtha*, the last distillate is received as such. The operation is carried on up to the point at which the distillate begins to show a little colour. Then the steam is stopped at once, and the operation finished. If the washing has been well done, the distillate remains colourless, and the end of the distillation must be judged of by other tests. Smell is a very distinct and characteristic test, but necessarily subjective ; naphthalene especially will thus be detected. Another criterion (in this case a certain one) is the specific gravity, which ought to be 0.900 for the last sample running out of the worm, or 0.880–0.887 for the whole of the naphtha. A further test is obtained by shaking up the naphtha ; only opalescent beads, instantly vanishing, ought to be formed, and no remaining froth. Moreover it ought not to be discoloured when exposed to the sunlight for several days ; it will then keep colourless in the dark for a long time.

The distillation of the 5- to 8- per-cent. burning-naphtha which can be got from the distillate up to 140°C . of the benzol-still (p. 263) takes a comparatively very long time. Hence it is often preferred not to distil it at all up to this point, but to mix the residue, remaining after getting out the solvent naphtha, with the fraction from the benzol-still boiling from 140° to 170° , which is distilled at once by open steam and yields merely solvent and burning-naphtha.

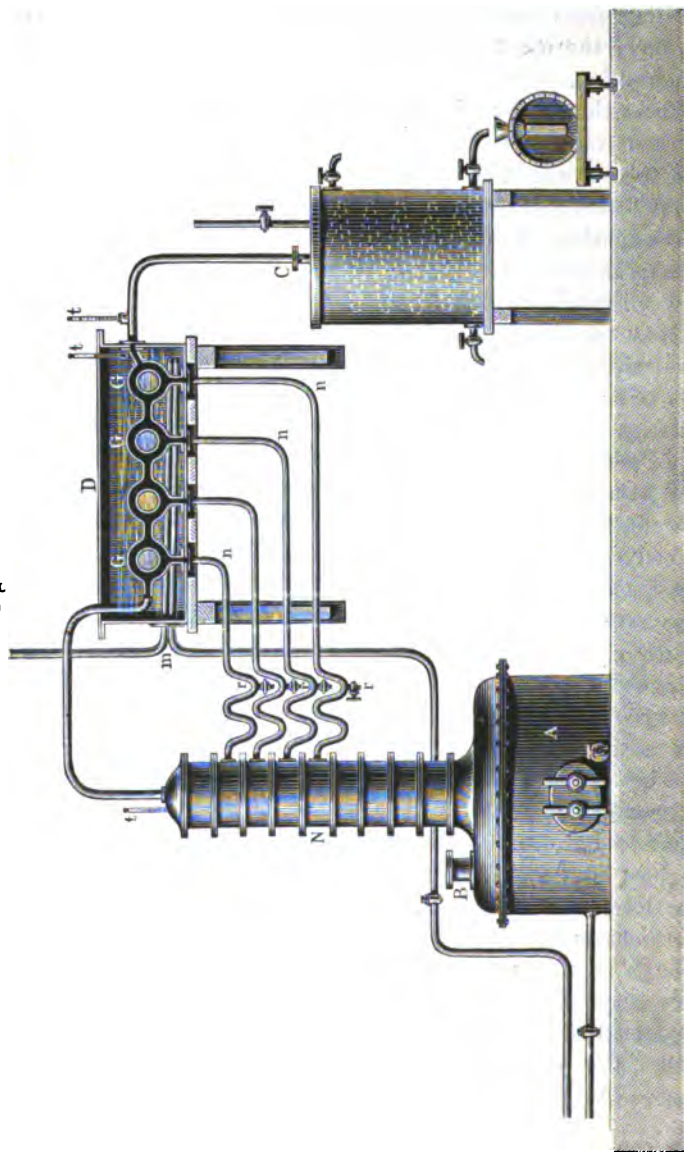
In all distillations by open steam the box for catching any liquid carried over (*v* in fig. 53, p. 267) is essential for protecting the distillate from discoloration; it should be emptied at least once per day; the caustic liquor in *b*, fig. 54, p. 270, must also be daily renewed.

From the product distilled up to 140° may be expected 60 or 70 per cent. of 50-per-cent. benzol, 20 or 25 per cent. of carburetted and solvent naphtha, 5 to 8 per cent. of burning-naphtha. The product distilled between 140° and 170° yields 25 to 50 per cent. best naphtha, 50 to 25 per cent. burning naphtha, and 25 per cent. residue in the still, which it is best to pass through the light-oil still, although it generally sinks in water.

Most tar-distillers make only 90- or 50-per-cent., sometimes 40-per-cent. benzol, solvent and burning-naphtha. Only exceptionally, and that mostly at the colour-works, is a *complete separation into benzene, toluene, xylene, &c.* aimed at. This can be effected by more perfect apparatus than those hitherto described, carrying out the principle of dephlegmation as completely as this has long been done in the rectification of spirit of wine. Mansfield proposed this already in 1847; but it seems that Coupier, in 1863, first carried it out for the purpose of isolating each of the hydrocarbons in a nearly pure state*. His apparatus is shown in fig. 55, on a scale of 1:50. A designates the lower reservoir (the still proper), to which is attached a steam-pipe (forming a coil inside), a man-hole, a discharge-cock, &c. B is the opening for feeding with crude benzol. The still is surmounted by the cast-iron rectification-column N, which will be described in detail below. The thermometer *t* is required for regulating the process. The heat of the steam-coil in A (the steam should be at a pressure of two atmospheres, or even more for the highest homologues) causes the liquid to boil. In the column A the least-volatile oils are condensed by the cooling action of the air and run back into A. The more volatile vapours pass into the trough D, where they are kept at such a temperature that the hydrocarbon of lowest boiling-point remains in the state of vapour, whilst all the higher-boiling ones condense and flow back into the still. For this purpose the vapours pass through the annular spaces of the condensers, placed alongside one another, whose walls

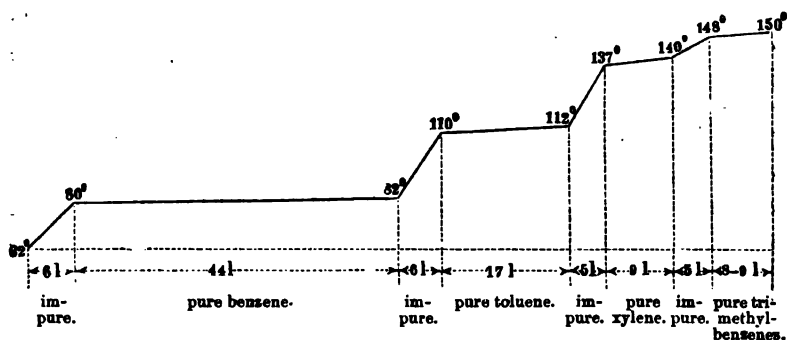
* Bulletin de la Société industr. de Mulhouse, 1866, p. 260; Dingler's Journal, clxxxi. p. 385.

Fig. 55.



are washed inside and outside by the liquid contained in D. If only benzene and toluene are to be separated in the pure state, the liquid in D may be water; for the temperature in D should be kept (by means of the steam-coil *m* and the thermometer *t*) at 60–70° for benzene (boiling-point 80°·5), and at 100° for toluene (boiling-point 111°). If xylene or trimethylbenzenes were to be obtained, D would have to be filled with a solution of ammonium nitrate (boiling at 164°), or with paraffin*. What condenses in the annular condensers G G, runs back to N through the pipes *nn*, whose bends prevent the passage of vapours from N to G G. It will be seen that the liquid first condensed enters the column higher up than that condensed afterwards. The taps *rr* serve for taking samples and testing the operation. The vapours issuing from the last condenser pass into the worm C, where they are completely condensed. If crude benzol is distilled, the water in D is first kept at 60° or 70°. When no more benzene comes out of C, the receiver is changed, and the temperature in D got up to 100°. At first a little of a mixture comes over; but soon pure toluene appears, which requires steam of 3½ atmospheres in A. When this ceases, the operation is usually stopped; but in case of need, xylenes and trimethylbenzenes can be isolated in a similar manner. Coupier has shown by the following graphical diagram the quantity of

Fig. 55 a.



principal and intermediate products obtained by his apparatus

* This would require steam of 6–7 atmospheres for the steam-coil in A; is it hardly ever done.

from 100 parts of crude benzol, boiling from 62° to 150° (say ordinary commercial 50-per-cent. benzol).

Hence 44 parts pure benzene and 17 pure toluene are obtained, and also :—(a) 6 parts first runnings, consisting partly of carbon bisulphide, amylene, &c., which may be utilized by adding it to the solvent naphtha; (b) 6 per cent. of an intermediate product between benzene and toluene, which is redistilled; (c) about 27 per cent. higher-boiling products which formerly went at once into the solvent naphtha, but from which now the xylene (9 per cent.) is sometimes separated.

According to Häussermann,* from 100 parts of commercial 90-per-cent. benzol, 6 or 7 parts of first runnings, 65 or 70 parts of pure benzene, and correspondingly less toluene are obtained. One hundred parts of tar yield about 0.6 pure benzene, 0.4 toluene, and 0.5 higher homologues.

Fig. 56.



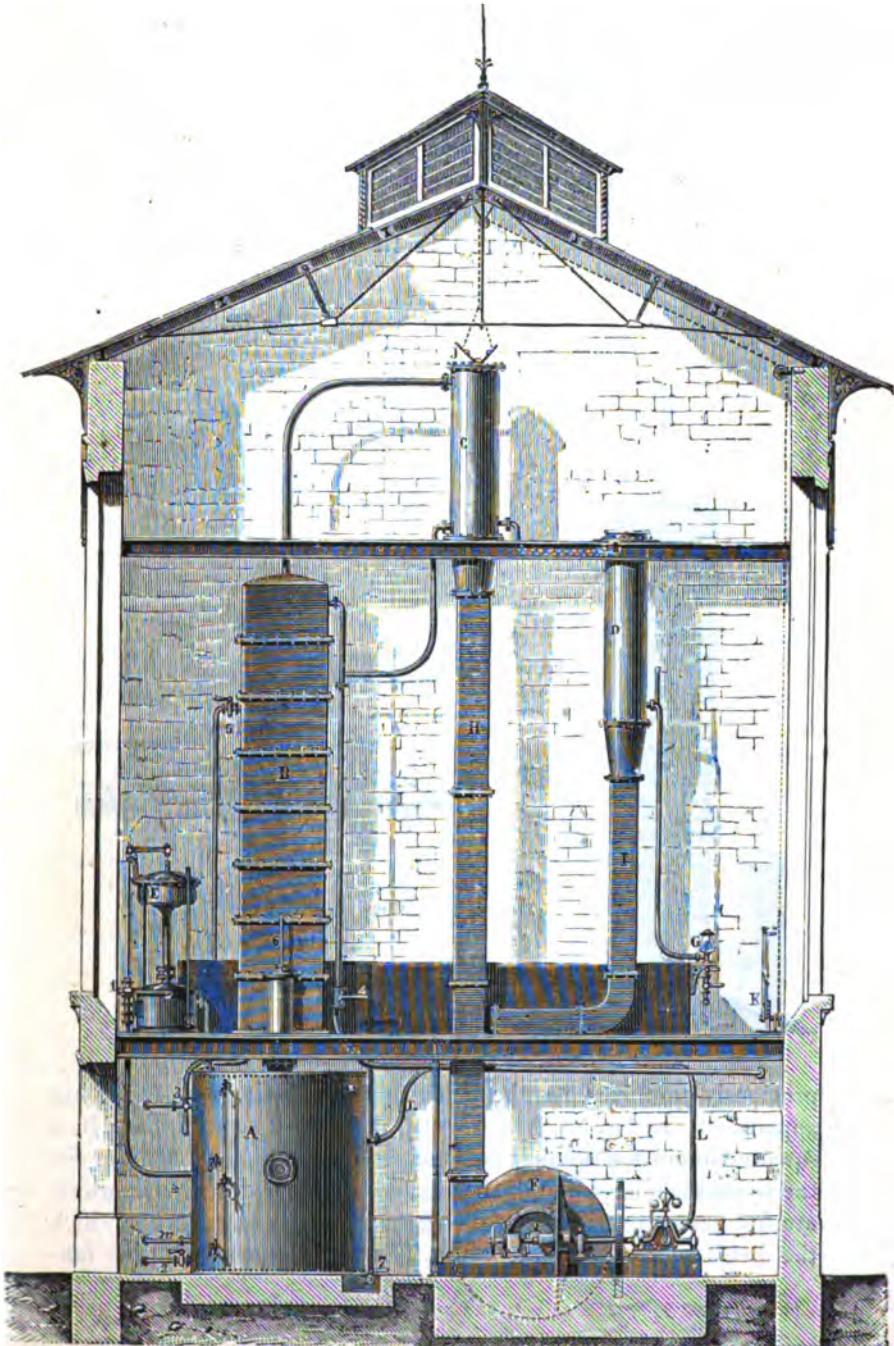
Fig. 57.



Figs. 56 and 57 show the plan and section of the compartments of the rectifying-column N on a scale of 1 : 25. The vapours rise in the pipes *g*, but are checked by caps *r*, and must find their way through the apertures and the liquid standing over them. That liquid, consisting of the portion of the vapours condensed by the cooling action of the air, gradually flows through the overflow-tubes *s* from one plate onto another. The labyrinth-partitions ("chicanes") *pp* cause the gas to remain in prolonged contact with the liquid, so as to precipitate the less volatile oils from the vapours, and to carry away by the heat of the latter the most volatile constituents of the liquid. The frequent repetition of this process in the 9 or 10 compartments of the column causes the fractionation to be much more thorough than even repeated rectifications without them would have made it.

* Industrie der Theerfarbstoffe, p. 18.

Fig. 58.



Coupier's apparatus does not seem to have been very much employed elsewhere; but the copper rectifying-apparatus of D. Savalle, fils, of Paris, enjoy special reputation for applicability to the hydrocarbons of coal-tar, and are largely employed by German tar-distillers even for 90- or 50-per-cent. benzol. Figs. 58-62 represent this apparatus. The condensation is, in this case, effected completely and exclusively by a current of air, the strength of which is regulated by a slide; there are also contrivances for regulating the steam pressure and for checking the speed of evaporation, as

Fig. 59.

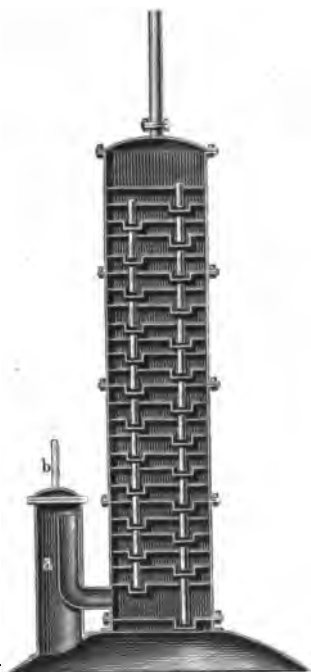
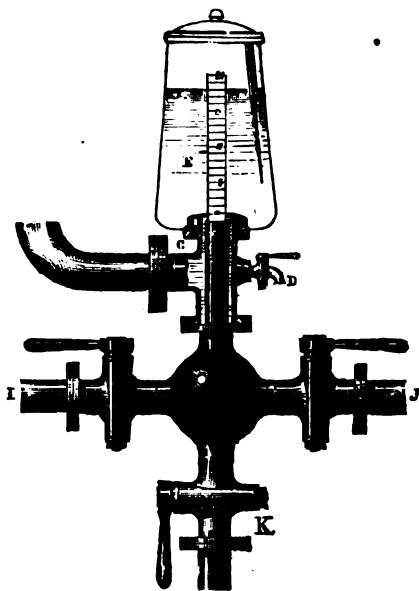


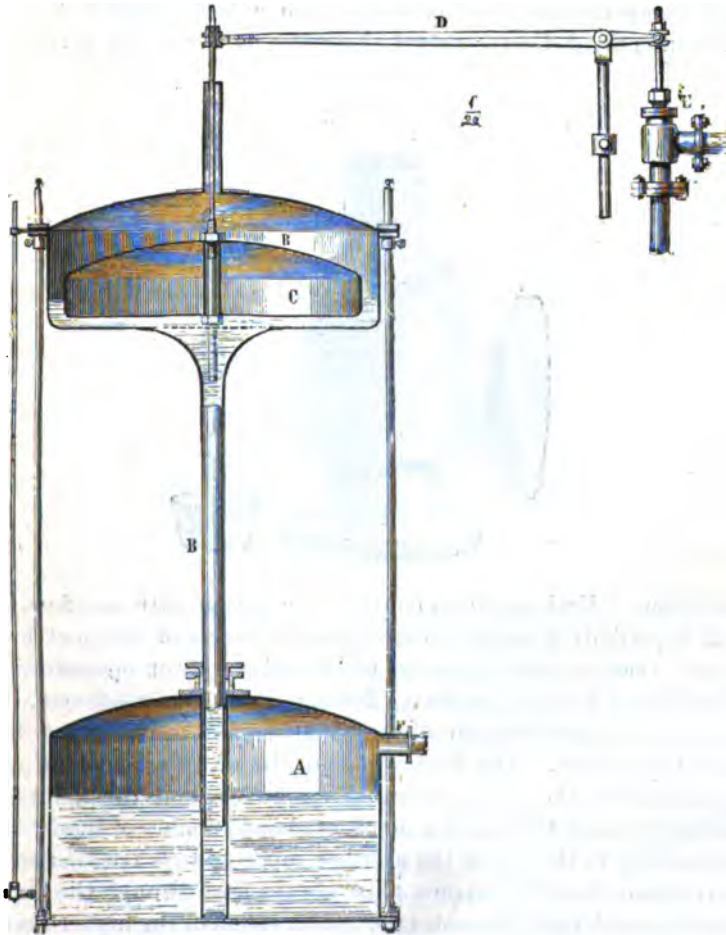
Fig. 60.



previously employed by the same firm for their spirit-rectifying apparatus. In fig. 58, A is the still, heated by a steam-coil; B, a square column for the first condensation; C, the air-condenser for the second condensation of the higher-boiling hydrocarbons which are not passed over into the distillate; D, the air-cooler, in which the distillate itself is condensed. The air is supplied by the fan-

blast F, through H to C, and through I to D. J is the slide which regulates the current of air in the condenser, by means of a chain and a graduated lever K. The liquid condensing in D passes

Fig. 61.

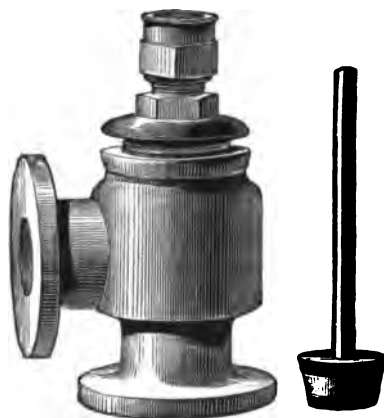


through the check-apparatus G for controlling the speed of the distillation. E is a regulator for maintaining a constant pressure in the apparatus throughout the distillation, L is the steam-engine

supplying the fan-blast ; 1, steam-valve of the regulator ; 2, condensed-water ejector ; 3, backflow tap of the column ; 4, purifying-tap of the same ; 5, discharge-cock of the upper part of the column ; 6, thermometer ; 7, tap for discharging and charging the still.

The inner arrangement of the column is shown in fig. 59. The vapours enter it by the cylinder *a*, divided by a vertical partition into compartments, and provided with a thermometer, *b*. The column is divided into several chambers by horizontal perforated

Fig. 62.



partitions. Each partition contains a perpendicular overflow-pipe which partially dips into a corresponding recess of the next lower plate ; these overflow-pipes are placed alternately on opposite sides. The higher-boiling products, flowing down the condenser, thus successively pass through all the chambers and ultimately go back into the column. The perforations of the plates are made of such diameter that the rising current of vapours prevents the liquid from falling through them, and a depth of about 2 inches of liquid (corresponding to the top of the overflow-pipes) always remains on the partitions : thus the vapours must always pass through the liquid, which considerably promotes the condensation of the higher-boiling products.

Fig. 60 shows the check-apparatus. The distillate from the cooler passes first into the annular space between the pipes C and F. The upper, graduated portion of the latter projects into the

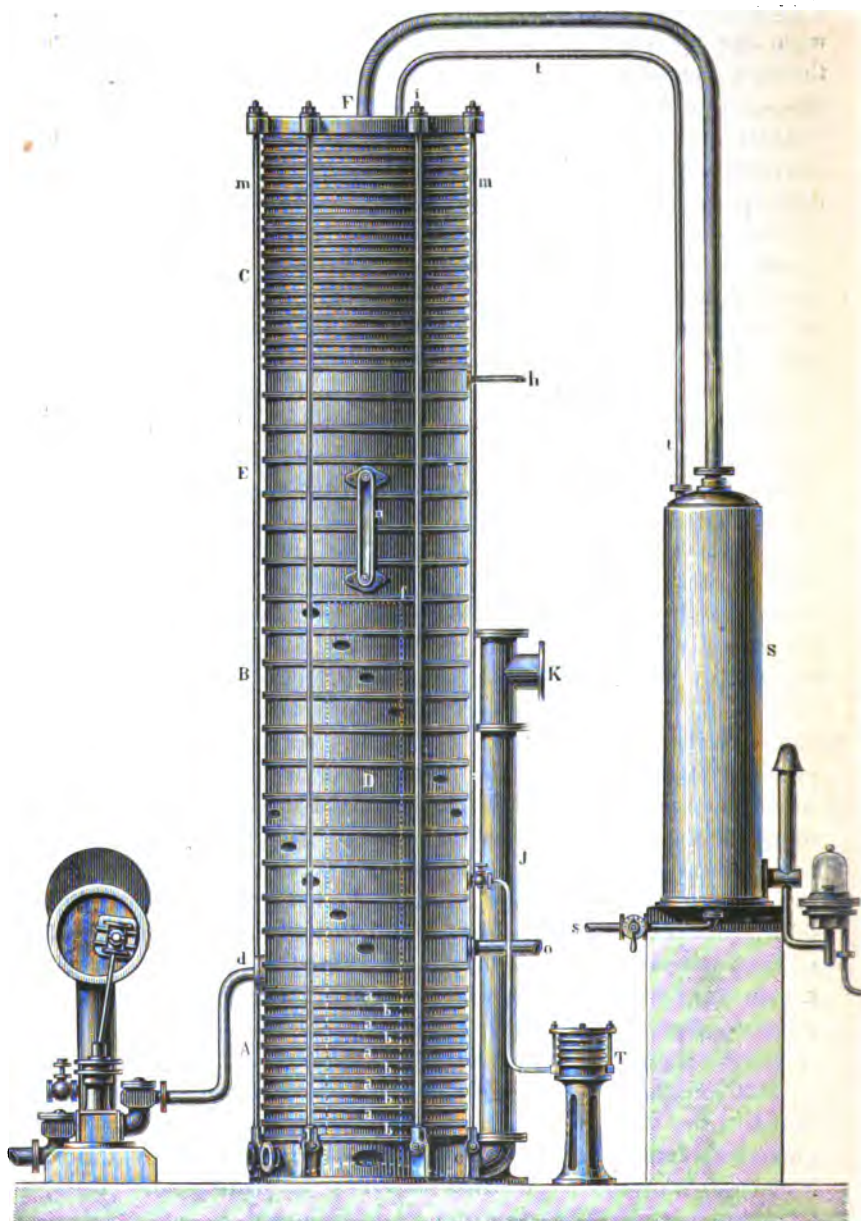
glass jar E, and has a small orifice at F. The space between C and F communicates with E. If the flow of the distillate is such that, with the pressure existing in the apparatus, it can run away through the orifice F, the liquid will not rise above this; but if the speed of flow is in excess of that, the liquid will rise from the annular space between C and F into the jar E. This will cause an hydraulic pressure, in consequence of which the distillate will pass more quickly through F. Thus a state of equilibrium will be produced; and it will be seen that the level of the liquid in the jar E, which can be read off on the graduation of F, depends upon the speed of flow of the distillate. Hence, conversely, the latter may be inferred from the former. The size of the orifice in F must of course be regulated once for all on starting the apparatus. The graduation on F is arranged so as to give the quantity of liquid passing hourly through the apparatus; and a glance at it suffices to show whether the proper quantity of distillate per hour is delivered—that is, whether the apparatus is in order or not. D is a tap for taking samples.

Fig. 61 shows the arrangement of the pressure-regulator. It consists of two superposed vessels connected by a pipe B. The lower vessel, A, is partly filled with water, and communicates through F with the rectifying-column. The upper vessel is provided with a float C, acting by the lever D upon the conical valve in E. The latter communicates both with the steam-boiler and with the steam-coil heating the still. As soon as pressure is produced in the apparatus, the water must rise in the pipe B, and, when the pressure has attained a certain degree, will enter the upper vessel and lift the float C. This depresses the valve E and checks the supply of steam. If by some accident, as choking up, the pressure in the still should rise too high, the regulator will shut off the steam entirely. By suitable adjustment it can be managed so that, in consequence of the action of the regulator, a certain pressure is never exceeded, which is important both for obtaining a constant product, and for preventing accident.

Fig. 62 shows the steam-valve, moved by the regulator.

Further details on Savalle's apparatus for rectifying spirit will be found in the *Bulletin de la Société d'Encouragement*, 1876, p. 657 (*Dingler's Journal*, cxxxi. p. 615), and in a pamphlet by Désiré Savalle, '*Appareils et procédés nouveaux de distillation*' (Paris, G. Masson, 1876, 223 pages and 48 diagrams).

Fig. 63.



The preparation of *chemically pure benzene* by crystallization, which is not a technical operation, has been mentioned on p. 38.

The apparatus described in the following, and shown in figures 63–66, was patented (by Siemens Brothers & Co., of Charlotten-

Fig. 64.

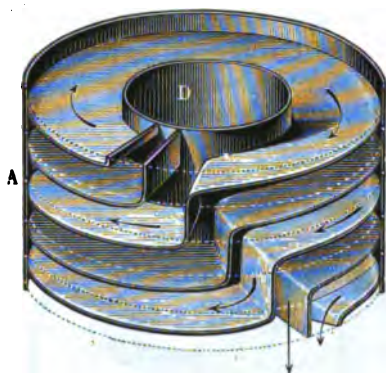
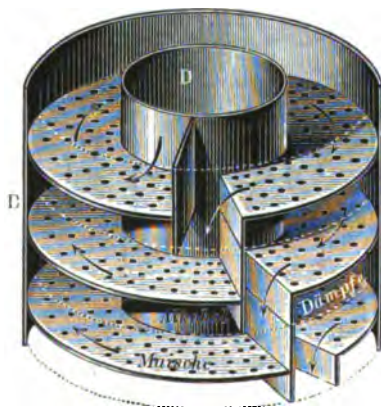


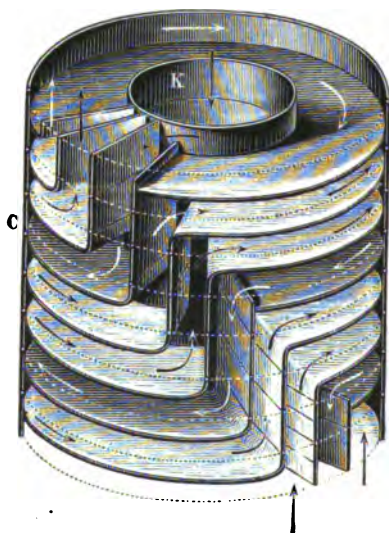
Fig. 65.



burg) originally for rectifying spirit (for which purpose 67 of them were already in use in February 1881), but, with a few slight modifications, is equally adapted for the rectifying of coal-tar oils. They construct 13 different sizes of the apparatus, for hourly out-

puts of from 200 to 1000 gallons, at from £200 to £550 cost, inclusive of auxiliary apparatus. The height of the column varies from 15 feet in the smallest to 37 feet 6 inches in the largest size. The apparatus is composed of three principal parts—the heater (A), the column (B), and the rectifier (C), all made of cast iron, joined by varnished pasteboard packing and bound together by the long bolts *mm*. In actual work the chambers, *bb*, of the heater A, as well as part of *c*, are full of hot residues; the chambers *aa* and the remaining part of *c* are filled with cold oils, which receive a preliminary heating, before passing into the column B, from being surrounded by the hot residues.

Fig. 66.



The oil is pumped into the heater at *d*, travels round the central tube D in the annular passages *aa*, descends into *c*, passes a portion of this vessel, enters the central tube D by a wide opening, rises up in D, and at *f* enters into the column B. This column consists of a number of chambers with a central tube open at top and bottom, and a perforated annular bottom. The space below the bottom receives the vapours rising from the liquid underneath; the space above receives the liquid to be rectified.

The liquid can only circulate by travelling in one direction round the central tube—but not quite round, a partition preventing this, whilst a lower opening gives communication with the liquid contained in the next lower chamber. During this passage the oils, circulating in the shape of a long ribbon, lose in the lowest part their more volatile matters by the heat of the steam acting in the copper coil *o*; but the same heat is always used over again for rectifying the contents of an upper portion of the stream, none of these portions getting mixed up together. Thus the evaporation of the more volatile matters takes place with a close approximation to completeness, and with the expenditure of very little steam. The residue, deprived of benzene &c., passes from the lower part of B into the heater, and in the chambers *b b* imparts its heat to a fresh quantity of oils in *a a*; ultimately it runs out continuously through the pipe J at K. The chambers *a a* and *b b* have sloping bottoms; both residues and fresh oils travel from the top downwards, so that no deposit can be formed (which is more important in distilling fermented wort than tar-oils). The space E serves for receiving any froth. The apparatus ought to be filled up to the liquor-gauge *n*.

The vapours from B pass into the rectifier, C, composed of a number of chambers in which the vapours are partially cooled by the surrounding water; the portion which is not liquefied passes at F into the condenser S, whilst the liquefied part collects at the bottoms of the chambers, and, so far as it is not evaporated again, ultimately flows back through an interior pipe into the column B. The cooling-water enters the rectifier at *i*, slowly circulates in it, and runs off hot at *h*. It is expedient to let the water first act in the condenser S, which it enters at *s*, and leaves at *t*, to enter the rectifier at *i*. The check test at T permits the control of the way in which the rectification is proceeding.

It is asserted that these apparatus require a minimum of steam and of cold water for complete volatilization of the lightest oils, that they are most easily managed, and combine comparatively small first cost with great durability, the material being cast iron.

Fig. 63 is an external elevation; fig. 64, an enlarged section of the heater; fig. 65, a similar section of the column B; fig. 66, a section of the rectifier.

Commercial Descriptions of Benzol and Naphtha.

The usual descriptions of the products from light tar-oils yield the following distillates (in percentages by volume), according to the authors' own tests :—

Commercial products.	Initial boiling-point.	88°	93°	100°	110°	120°	130°	138°	149°	160°	171°
90-per-cent. benzol	82	30	65	90							
50-per-cent. benzol	88	...	13	54	74	90					
Toluol	100	56	90					
Carburetted-naphtha ...	108	1	35	71	84	97		
Solvent naphtha	110	17	57	71	90		
Burning-naphtha	138	30	71.5	89

The temperatures were all measured with the thermometer-bulb just submerged in the liquid, at the beginning of the distillation.

Häussermann* quotes the following results :—

At.....	85°	90°	95°	100°	105°	115°	120°	135°	140°	145°	150°	170°	180°
90-per-cent. benzol	20	72	84	90	95	98							
50-per-cent. benzol	...	5	30	50	64	81	94						
Solvent naphtha	6	48	72	85	92	95

According to another statement, made to the author by an English tar-distiller, the ordinary results are :—

At.....	100°	120°	130°	160°	Sp. gr.
90-per-cent. benzol	90	0.885
50-per-cent. benzol	50	90	0.880
30-per-cent. benzol	30	90	0.875
Solvent naphtha	20	90	0.875
Burning-naphtha	30	0.885

According to Chateau†, in France (1864) the following three classes of benzol were distinguished :—

(a) *Very light benzol*, boiling between 80° and 100°. 3 or 4 cubic centimetres of this, added to 5 or 6 c. c. of concentrated

* Industrie der Theerfarbstoffe, pp. 13 & 14.

† Bulletin de la Société Industrielle de Mulhouse, 1864, p. 97.

oil of vitriol, colour it yellow in the cold without shaking; on being shaken, it first turns orange, then red; the benzol itself remains colourless. On heating, the acid turns much darker, and the benzol turns first yellow, then orange. If the mixture be poured into 10 times its bulk of water and the whole shaken up, a dirty-pink liquid is observed. On standing, a yellow, somewhat muddy, liquid separates.

(b) *Light benzol*, distilling between 100° and 120° . In the cold the acid is turned yellow, and on shaking passes through orange into dark red, the benzol remaining colourless. On heating, the acid turns darker, the benzol first golden yellow, then orange-red. On the addition of water a greenish-yellow muddy liquid is produced; the benzol settling from it is coloured similarly, but lighter.

(c) *Heavy benzol*, distilling between 120° and 140° . In the cold the acid turns green, and on shaking passes into blood-red; the benzol is colourless. On heating, the acid turns darker, the benzol yellow, then orange, at last dark red like the acid. On addition of water a dirty grey-green liquid is produced; the liquid floating above is yellow.

These reactions do not seem to possess much practical value.

Allen* gives the following results of distilling the commercial products in the usual way:—

	Very good first runnings (once-run naphtha).	Good 90- per-cent. benzol.	Scotch 90- per-cent. benzol.	50-90- per-cent. benzol.	30- per-cent. benzol.	Solvent naphtha.	Mixture of 70 pure benzene and 30 toluene.
Spec. grav.	0.882	0.873	0.880	0.875	0.877	0.880
First drop collected at... °	82 ° ° ° ° °	85.4 °
10 per cent. " " "	96	83½	84½	94	97	128½	86.6
20 " " " "	99½	84½	85	95	98	130	87.2
30 " " " "	102	85	85½	96½	99½	132½	87.8
40 " " " "	107	85½	86½	98	101	135	88.8
50 " " " "	111	86½	87½	100	104	137	89.8
60 " " " "	119	88	89	102½	106	140	91.4
70 " " " "	128	89½	91½	106	109½	143½	93.2
80 " " " "	145	92½	94½	110½	113½	148½	96.2
90 " " " "	170	120	120	156	102.6
92 " " " "	100
95 " " " "	107.0

* Commercial Organic Analysis, vol. ii. p. 87.

According to the same author a good sample of 90-per-cent. *benzol* should not begin to distil under 80°, and should not yield more than 20 to 30 per cent. at 85°, or much more than 90 per cent. at 100°. An excessive distillate, *e.g.* 35 to 40 per cent. at 85°, indicates a larger proportion of carbon bisulphide (see below) or light hydrocarbons than is desirable. The actual percentage composition of a 90-per-cent. *benzol* of good quality is about 70 per cent. of benzene, 24 of toluene, a trace of xylene, and 4 to 6 of carbon bisulphide and light hydrocarbons. It should be colourless and free from opalescence. The specific gravity of English 90-per-cent. *benzols* usually ranges from 0·880 to 0·888 at 15°·5; that of Scotch *benzols* (which contain little carbon bisulphide, but a considerable proportion of light hydrocarbons) is often as low as 0·871. 50-90-per-cent. *benzol* is the same as is called here 50-per-cent. *benzol*, *viz.* a product of which 50 per cent. by volume distils over at a temperature not exceeding 100°, and 40 per cent. more below 120°. 30-per-cent. *benzol* yields 30 per cent. at 100°, and 60 per cent. more between 100° and 120°; it consists chiefly of toluene and xylene. *Solvent naphtha* gives from 8 to 30 per cent. distillate below 130°, and about 90 below 160°; it consists chiefly of toluene and xylene, with notable quantities of cumene and still higher homologues, and several per cent. of naphthalene (in this case the author must demur; there must be very little toluene in this product; "cumene" does not occur in coal-tar at all, but only isomers of this body; and higher homologues have been neither proved to exist in coal-tar nor is their presence theoretically probable: compare p. 36).

A substance occurring just in the strongest *benzol*, to which attention has only quite recently been drawn, is *carbon bisulphide*. This body has been indicated, amongst others, by Vincent and Delachanal*. Watson Smith (*priv. comm.*) has observed in English *benzols* up to 5 per cent. carbon bisulphide, which gave rise to complaints. The occurrence of this substance is easily accounted for, all conditions for its formation being present in the gas-retorts, *viz.* red-hot carbon and vapour of sulphur (from the pyrites which always occurs in coal); neither do the ordinary purifying agents, *viz.* sulphuric acid and alkali, remove it. It is true that a good deal of the carbon bisulphide existing in raw

* *Compt. Rend.* lxxxvi. p. 340.

tar will remain uncondensed during the distillation; but some of it must pass into the lightest oils, and the more the more perfect the condensing-plant is. Its smell does not betray it, even when 20 per cent. is mixed with benzol, which is much in excess of any thing ever occurring in practice. 5 per cent. CS_2 in benzol makes no difference whatever in the smell; and even the first distillate smells of benzene, not of CS_2 . But a safe test is afforded by the specific gravity, which is much raised by CS_2 . Watson Smith, on adding 5 parts of CS_2 to 100 of benzol of sp. gr. 0.875, yielding 20 per cent. below 100° , got on distilling 35 per cent. below 100° , of sp. gr. 0.917. By employing a Linnemann's fractionating apparatus or the like, probably nearly pure CS_2 would have been got out. We shall describe the tests for it later on.

To distinguish coal-tar benzol or naphtha from petroleum or shale-spirit &c., which are also frequently called "benzoline, naphtha," &c., and which may easily occur as adulterations of the former, is not difficult. Both products can be at once distinguished by their smell, if unmixed; but in mixtures the smell of coal-naphtha prevails even over a very large addition of petroleum or shale-spirit. But the specific gravity affords a never-failing test: with coal-naphtha it is always above 0.870 at 15° , with petroleum spirit &c. below or at most very little above 0.700. Very distinct is the reaction with nitric acid, which at once acts upon the aromatic hydrocarbons of coal-tar, but hardly at all upon the fatty compounds of petroleum or paraffin oil.

The following useful synopsis of the characters of the two kinds of products has been made by A. Allen* :—

Petroleum spirit, Benzoline, Benzene.

1. Consists of heptane (C_7H_{16}) and its homologues.
2. Heptane contains 84.0 per cent. of carbon.
3. Commences to boil at $54\text{--}60^\circ \text{C}$.
4. Specific gravity at $15^\circ\text{--}5$ about 0.69 to 0.72.
5. Smells of petroleum.
6. Dissolves iodine, forming a solution of a raspberry-red colour.
7. Does not sensibly dissolve coal-tar pitch, and is scarcely coloured by it even on prolonged contact.

Coal-tar Naphtha, or "Benzol."

1. Consists of benzene (C_6H_6) and its homologues.
2. Benzene contains 92.3 per cent. of carbon.
3. Commences to boil at about 80°C .
4. Specific gravity about 0.880.
5. Smells of coal-tar.
6. Dissolves iodine, forming a purple-red liquid of the tint of an aqueous solution of potassium permanganate.
7. Readily dissolves coal-tar pitch, forming a deep-brown solution.

* Chemical News, xl. p. 101.

- | | |
|--|--|
| <p>8. When shaken cold with one third of its volume of fused crystals of absolute carbolic acid, the latter remains undissolved and forms a separate lower stratum.</p> <p>9. Requires two volumes of absolute alcohol, or 4 or 5 volumes of methylated spirit of sp. gr. 0.828, for complete solution at the ordinary temperature.</p> <p>10. Warmed with four measures of nitric acid of sp. gr. 1.45, the acid is coloured brown, but the spirit is little acted on and forms an upper layer.</p> | <p>8. Miscible with absolute carbolic acid in all proportions.</p> <p>9. Miscible with absolute alcohol in all proportions. Forms a homogeneous liquid with an equal measure of methylated spirit of sp. gr. 0.828.</p> <p>10. Completely miscible with four measures of nitric acid of sp. gr. 1.45, with great rise of temperature and production of dark-brown colour. A portion of the nitrobenzene produced may separate out as the liquid cools.</p> |
|--|--|

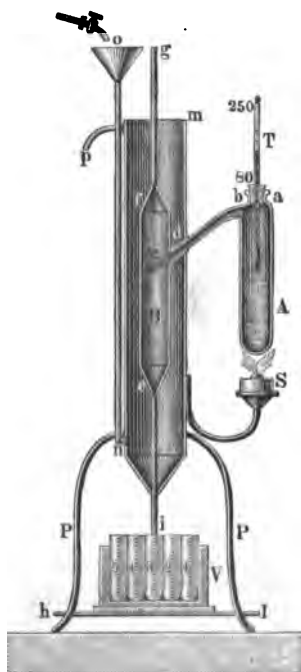
No. 10 is capable of giving quantitative results in separating the two kinds of oil. The oil to be tested is treated with nitric acid of sp. gr. 1.45 in a small flask with an inverted condenser. When action has nearly ceased, the whole is poured into a narrow graduated tube; the measure of the upper layer indicates approximately the amount of petroleum spirit present. If the proportion of benzene is considerable, the nitrobenzene formed may not remain completely dissolved in the acid, but form a layer of dark-brown colour below the stratum of petroleum spirit. Nitrobenzene and petroleum spirit are readily miscible in the absence of nitric acid; but agitation with strong nitric acid dissolves out the nitrobenzene, a portion of which may rise and form an intermediate layer as above described.

For testing benzol by fractional distillation, usually ordinary glass retorts or fractionating-bulbs are employed, as fig. 50, p. 253. In this case the position of the thermometer is of great importance (pp. 252 & 296), and also in other respects different results may be obtained in apparatus of unequal construction. On this account, and on account of the fragile nature of glass retorts, Regnault, at the instance of the French Government, constructed a normal apparatus*, which is shown in section in fig. 67. A is a cylindrical copper retort with a neck, *a*, and the bent vapour-tube, *b c*. The latter fits tightly into the lateral tubule *d* of the condenser B. This consists of a brass cylinder *e f*, ending at top and bottom in narrow metal tubes *g* and *i*, and fixed air-tight in a wider metal cylinder *m n*. Into the latter enters a stream of water through *o* at the bottom and leaves at the top at *p*. It stands on a tripod P P,

* Ann. Chim. Phys. lxxiii. p. 409.

to which a horizontal frame *hl* is attached. In the latter slides a carrier *V*, containing five glass tubes, closed at the bottom and divided into cubic centimetres, each of which can be thus brought under the outlet-pipe *i* of the condenser. By means of a pipette the retort is charged with 100 c. c. of oil, which ought not to occupy much more than a third of it. The thermometer *T* is fixed in

Fig. 67.



the tubule *a* so that its bulb does not dip into the liquid, and that the 80th degree comes out very little above the cork. The distillation is carried on by the gas- or alcohol-flame *S*. The ordinary fixed points for changing the receivers 1 to 5 are 100°, 120°, 140°, 160°, and 180°. It is clear how easy is the changing of the receivers and the reading-off of the volume of each fraction. The condenser is cooled by means of water.

At the tar-works and at the buyer's laboratories, glass retorts are employed for testing benzol. Frequently differences of opinion occur between buyer and seller, chiefly caused by the fact that it

is not usual in the English trade to place the thermometer in the only proper position, as shown in the diagram fig. 50, p. 253, but to let it dip more or less into the liquid. Further deviations are caused by differences in the size of the retorts and the speed of the distillation. The following detailed directions by W. W. Staveley* are intended to produce a uniform result ; but this would involve their being accepted everywhere as binding, which is far from being the case. 100 c. c. of the sample is to be put into an ordinary 6-ounce stoppered retort, connected with a Liebig's condenser whose condensing-tube is 1 inch wide (?) and 30 inches long. The thermometer is so fixed in the retort that its lowest point is $\frac{3}{8}$ inch from the lowest portion of the retort. Heat is applied by means of a Bunsen rose burner (fig. 68), in such a manner that the

Fig. 68.



distillate runs in separate drops into the 100-c. c. burette employed as the receiver. A moment before the desired temperature is reached the lamp is removed, whereupon the thermometer rises to the proper point ; and the reading-off is made as soon as the benzol has ceased to drop from the condensing-tube. The contents of the retort, after cooling, are poured into the burette ; and the loss, if any, is added to the percentage of the distillate. New corks absorb benzol, and hence are not to be recommended ; neither are new clean retorts suitable, unless a few grains of brick are introduced.

* Chemical News, xliii. p. 70.

Best of all are retorts which, having been used for some time, have a slight coating of carbon inside.

Allen's prescriptions (*l. c.* p. 84) are very similar to this; but he employs a retort holding 8 ounces of liquid, with the end of the thermometer $\frac{3}{8}$ inch from the bottom of the retort, and a condenser 15 to 18 inches long.

It has been pointed out* that the benzol test is affected by differences in the barometric pressure. But the assertion, made at the same time, that for each $\frac{1}{10}$ inch lowering of the barometer 0.8 per cent. more is found than at the normal pressure, is evidently exaggerated. W. Thomson† recommends immersing the distilling-vessel entirely in a copper water-bath, so that the quantity passing over will be ascertained independently of the shape of the vessel, the state of the barometer, &c.; then the water might be siphoned off, and the copper box used as an air-bath for the higher temperatures. But it is here overlooked that the temperature inside the retort is several degrees below that of the water- or air-bath. In any case the water-bath would have to be brought, by the addition of common salt or the like, to such a temperature as to raise that inside the retort to 100°.

In order to avoid the influence of carbon bisulphide on the testing of benzol, which frequently leads to awkward irregularities (compare the statements of Watson Smith, p. 292), Nickels‡ treats the benzol twice with 10 per cent. by volume of a hot saturated solution of caustic potash in absolute alcohol, agitates for two hours, filters from the precipitate of potassium xanthate, removes the alcohol from the filtrate by twice washing with its own volume of water, removes the water suspended and dissolved by agitating with a little plaster of Paris, and distils as usual. Thus much more constant results are obtained than without that purification; the benzol now shows a lower specific gravity (0.882 or 0.880, instead of 0.885), and is quite free from alliaceous smell.

If the object of testing benzol is not to conform to an arbitrary commercial standard, but to ascertain its real composition, the common retort or fractionating-bulb ought to be replaced by a more perfect apparatus for fractional distillation, *e. g.* Linnemann's three-bulb tube, fitted with platinum-gauze cups, which is also

* Chemical News, xliii. p. 93.

† *Ibid.* p. 115.

‡ *Ibid.* pp. 148, 250.

recommended by Allen (*l. c.* p. 87). This author quotes the following results, obtained by Mr. B. Nickels from the same benzol (A, when distilled in an 8-oz. retort in the ordinary way; B, after removing the carbon bisulphide in the manner described on p. 297; C, when the *purified* benzol was distilled in a three-bulb apparatus instead of in an 8-oz. retort) :—

	A. Commercial 90- per-cent. benzol in 8-oz. retort.	B. A after being purified from CS ₂ in 8-oz. retort.	C. B distilled in flask with three- bulb apparatus.
Spec. grav. at 15°·5 ...	0·884	0·881	0·881
First drop distilled at	79·5	83·4	81·25
5 per cent. " "	84·2	84·3	82·0
10 " " "	84·0	85·0	82·8
20 " " "	85·0	85·8	83·0
25 " " "	85·4	86·4	83·5
30 " " "	86·4	87·1	84·7
40 " " "	88·0	88·3	85·3
50 " " "	90·0	90·0	86·5
60 " " "	93·0	93·0	89·3
70 " " "	100·0	100·0	100·0
80 " " "	112·4	111·8
90 " " "			
95 " " "			

By operating on 300 c. c. of the same sample, removing the carbon bisulphide by alcoholic potash, and several times repeating the process of fractionating with the three-bulb apparatus, Mr. Nickels obtained the following results as indicative of the proximate analysis of the benzol tested :—

	per cent.
Carbon bisulphide	1·5
Light hydrocarbons, sp. gr. 0·872 (not nitrifiable, probably chiefly amylene and acetonitrile)	3·5
Benzene, sp. gr. 0·885, distilling within a range of 2 degrees	78·4
Toluene, sp. gr. 0·8715, distilling within 2 degrees	16·6
	<hr/> 100·0

It is very desirable that the present empirical and conventional mode of benzol-testing should be replaced, at any rate in important cases, by the above scientific treatment.

Testing of Crude Benzol (first Runnings &c.) for Final Products.

The following rules are taken from the author's own practice. They are purely empirical; but by means of them the results to be expected on the large scale can be very approximately inferred from the laboratory distillations, which will take hardly a quarter of an hour.

1st. 100 c. c. of the oil is distilled from a glass retort or fractionating-flask, and the distillate collected, (a) up to 140° , (b) from 140° to 170° ; on each occasion, just as the required temperature is attained the lamp is withdrawn, and the oil contained in the condenser is allowed to drain off before the receiver is changed; this makes a difference of several per cent. Suppose we have got 68 c. c. up to 140° and 86.5 c. c. up to 170° ,—

2nd. The first distillate, in this case 68 c. c., is rectified, and that which passes over up to 100° is collected, allowing the oil to drain after removing the lamp. Suppose this to be 24 c. c. This figure, multiplied by 2, gives the quantity of 50-per-cent. benzol to be expected; in this case it is 48 parts from 100 parts of the crude oil.

3rd. The product (a) of the first distillation (up to 140°), in this case 68 c. c., less the 50-per-cent. benzol found according to rule 2, in this case 48 c. c., gives the volume of best naphtha, i. e. $68 - 48 = 20$.

4th. The total product of the first distillation up to 170° , in this case 86.5 c. c., diminished by 15 per cent. for loss by purification (washing) and distillation, and by the quantities of 50-per-cent. benzol and best naphtha found according to rules 2 and 3, gives the quantity of burning-naphtha. In this case, $86.5 - 13 = 73.5$; $73.5 - 68 = 5.5$ parts for 100 crude naphtha. (A loss of 15 per cent. may be regarded as the maximum; with careful work it does not exceed 10 per cent.)

5th. The difference is the residue going to creosote oil. Thus in our case we find the following total:—

48	parts 50-per-cent. benzol,
20	„ best naphtha,
5.5	„ burning-naphtha,
15	„ loss,
11.5	„ creosote oil.
<hr/>	
100.0	

If less volatile oils have to be tested, 200 or 300 c. c. are distilled up to 180° , and the residue is submitted to exactly the same operations and calculation-rules as have just been described.

Storage and Carriage of Benzol &c.

For storing benzol and naphtha, only wrought-iron vessels are suitable; they may be of any shape and size. Since tar-oils pass through the joints much more easily than water, both as liquids and as vapour, and since their vapours form with air easily inflammable or even explosive mixtures, the store-tanks must be constructed with special care and must be protected against any contact with fire. They are put together in as large plates as possible, to lessen the number of joints; and these are very carefully riveted and caulked. Only first-class workmanship will ensure that no evaporation takes place. The tanks are painted outside with good tar varnish (p. 154), but preferably not until the joints have somewhat rusted and thus have become tighter. They are provided with a hole for filling them, a man-hole, and two taps—one a little above the bottom for the ordinary filling of the sending-out vessels, the other in the bottom itself for occasionally drawing off any water and mud. The tanks are mostly placed on pillars high enough to fill the casks directly. But at some places tanks placed in the open air, and partially underground, are preferred, on account of the diminished danger of fire. In any case, for the same reason, the benzol storehouse ought to be at some distance from any fireplace; and it is best to employ an open shed for it. Lighting it is mostly unnecessary; in case of need this can be done only from the outside by means of reflectors.

The carriage of benzol is effected in good oak casks, *e. g.* spirit-puncheons, preferably made tighter by washing with a dilute solution of glue, like petroleum-barrels; but still better are tightly riveted iron casks.

For the momentary stoppage of leaks soap can be employed, which is not acted upon by naphtha; but it does not stand any considerable pressure. Glue, too, is not acted upon.

Applications of Benzol and Naphtha.

Commercial benzol is most extensively employed in the manufacture of colouring-matters, which is quite outside the scope of

this treatise. It is first converted into nitro-compounds. For this purpose 90-, 50-, 40-per-cent. benzol &c. are manufactured; quite recently also xylene, which is made from solvent naphtha in Savalle's columns (p. 282). The purest benzene is employed for manufacturing "huile de mirbane," a substitute for oil of bitter almonds. Benzol also very frequently serves as a solvent, both in the manufacture of colours and elsewhere. Of the greatest importance is its preeminent dissolving-power for fatty matters, upon which is based its extensive employment as a detergent; but petroleum "benzin" largely competes with coal-tar benzol in this respect. 90-per-cent. benzol serves for preparing the finest japans and varnishes, *e.g.* for photographic purposes. Of other applications of benzol we will only mention that for extracting iodine* (which has hardly ever been practised) and in making beet-root sugar †.

It is reliably estimated ‡ that the German colour-works consume monthly 1020 tons of benzol, nine tenths of which comes from England. Of this about two thirds is benzene, one third toluene. The employment of xylene in 1880 amounted to from 4 to 6 cwt. per diem.

The oils distilling just after benzol are very well adapted for *carburating gas*, *i.e.* for increasing its illuminating-power by the vapours of hydrocarbons; this is favoured by their low price and not too high degree of volatility. Whether carburating the gas is a profitable process or not, cannot be decided generally, but only in each special case, by taking into account the illuminating-power and price of the gas, and the price of the carburating naphtha. Coal-tar naphtha is much better adapted for this than petroleum spirit, on account of its larger percentage of carbon. That poor gas can be very much improved by carburating is beyond any doubt; but it is another question whether it is not more economical to make richer gases to begin with. The question is certainly not decided by the fact that some eminent gas-engineers have pronounced against carburation as a plaything or the like; for they are interested parties, and even the miscarriage of very many attempts does not refute the opinion that in other conditions the result would be favourable.

This subject was treated *in extenso*, and decided in favour of the principle of carburation, in 1865 by Dr. Letheby §. We shall

* Wagner's Jahresh. 1866, p. 182.

† *Ibid.* 1874, p. 674.

‡ Chemische Industrie, 1880, p. 416.

§ Chem. News. xi. p. 276.

content ourselves with enumerating some inventors of carburating-apparatus, including those for producing illuminating-gas from air and inflammable vapours—Mansfield¹, Rolands², Longbottom³, Lacarrière⁴, anonymous⁵, Brooman⁶, Gloessiner and Farenne⁷, Evans⁸, Mongrue⁹, Wells and Myers¹⁰, Reissig¹¹, Philipps¹², Jungling¹³, Parody¹⁴, Young and Kitt¹⁵, Bizot, Akar & Co.¹⁶, Fogarty¹⁷ (whose Excelsior Gas-Machine, for air carburated with gasoline, is highly spoken of), Hoyer & Studelmann¹⁸, Livesey & Kidd¹⁹, Stephan²⁰, Anders²¹, Richter & Triebel²².

In England, according to the index of patents, in the years between 1859 and 1866 not less than 151 patents were taken out for carburating gas. What has been said on p. 242 et seq. on carburation by naphthalene should also be recalled to mind.

Dr. Letheby's specification, which had been adopted by the London lighting authorities (p. 275), must yield a product essentially consisting of xylene. He did not assume this to act better than benzene or toluene; but he selected that product because it was not then employed at colour-works and consequently was lower in price. By Knublauch's investigations²³ it has been ascertained that, in fact, benzene, for equal weights, imparts the greatest illuminating-power to gas, and that the higher homologues only act in proportion to their molecules, only the carbon of the benzene nucleus being set free in a luminous form, whilst that of the methyl groups is burned directly to carbon dioxide.

If the products from crude benzol beyond toluene cannot be employed for lighting-purposes, they are all sold together as *solvent*

¹ Patent No. 11960, Nov. 11, 1847.

² Patent No. 1210, May 28, 1855.

³ Patent No. 660, March 20, 1854.

⁴ Bull. Soc. d'Encouragement, Mai 1857, p. 21.

⁵ Wagner's Jahresh. 1861, p. 683.

⁶ Patent No. 2770, Oct. 14, 1862.

⁷ Patent No. 67, Jan. 9, 1862.

⁸ Patent No. 2618, Oct. 19, 1861.

⁹ Patent No. 731, March 17, 1862.

¹⁰ Patent No. 2998, Nov. 22, 1865.

¹¹ Journal für Gasbeleuchtung, 1865, p. 396.

¹² Wagner's Jahresh. 1870, p. 733.

¹³ Bull. Soc. Chim. 1873, xx. p. 331.

¹⁴ *Ibid.* p. 335.

¹⁵ English patent, April 3, 1872.

¹⁶ French patent No. 94,576, April 12, 1872.

¹⁷ Journal für Gasbeleuchtung, 1874, p. 248.

¹⁸ German patent No. 4723.

¹⁹ German patent No. 2075.

²⁰ Ditto, No. 3856.

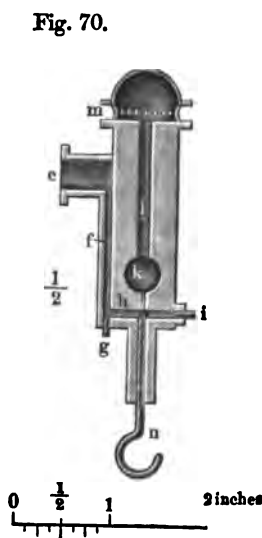
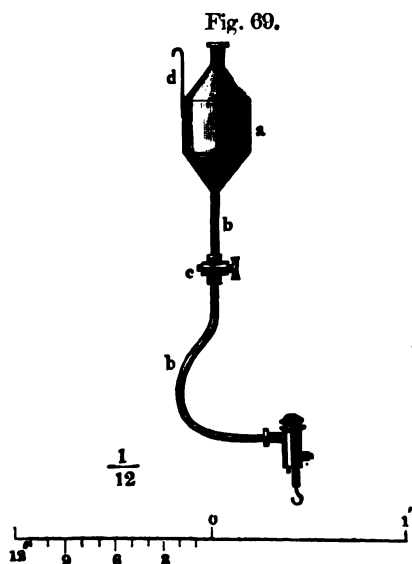
²¹ Ditto, No. 11,107.

²² Ditto, No. 12,150.

²³ Ber. d. deutsch. chem. Ges. 1881, p. 240.

naphtha for india-rubber, fatty matters, &c. What are the special requirements of English india-rubber-manufacturers, we have seen on p. 276. Their process itself has been described by Kniess*. Heeren† gave a table of the solubilities of different descriptions of india-rubber in "benzol," which shows variations of from 6 to 25 parts of india-rubber to 100 of "benzol." But whether he means pure benzene, or commercial benzol, or solvent naphtha, does not appear.

The last of the products is *burning-naphtha*. Coal-tar naphtha, whether pure or mixed with petroleum spirit, is not adapted for burning in ordinary lamps or at all in closed rooms, but merely for special lamps, without wick or chimney, which do their duty even in strong wind and rain, and hence serve for lighting factories, courtyards, booths at fairs, &c. in lieu of gas. Good naphtha, no doubt, gives a very fine white light. Figs. 69 and 70 show a suitable lamp for this purpose (Holliday's patent). Fig. 69 is the lamp



itself, on a scale of 1 : 12 ; fig. 70, the burner, on a scale of 1 : 2. *a* is the vessel for naphtha, from which a thin tube *b* leads downwards ; the cock *c* regulates the outflow ; the tube *b* is almost entirely filled

* Dingle's Journal, cxxxviii. p. 442.

† *Ibid.* cxxxi. p. 391.

up by a round wick, which extends nearly to the burner, and of which the sole purpose is to make the outflow of the naphtha gradual. The hook *d* serves for hanging up the lamp. In the burner we notice the lateral tube *e*, communicating with *b*, and introducing the naphtha. This flows downwards in the narrow channel *f*, which is closed by the thin screw *g*, the channel *h* being closed by *i*. The naphtha must rise from *h* in the fine central channel, leading to a hole *k* across the burner. Here it would run off, if the burner had not been previously heated sufficiently to evaporate it at once. The vapour, mixed with the air entering at *k*, rises in the central channel *l*, issues through the holes in the burner-head, and, on being lighted, produces a star-shaped flame. The draught generated by this suffices for preventing the naphtha vapour from issuing into the open air, instead of into the channel *l*. The screw *n* permits regulating the orifice of the fine channel between *h* and *k*. Here also a small cup may be fixed for some naphtha to be lighted in order to effect the first heating of the burner, the tap *c* being then closed. Otherwise the burner-head is put into some fire till it is warm enough. When this is the case, the tap *c* is opened, the vapour issuing out of the holes *m* is lighted, and the size of the flame regulated by *c*. Once lighted, the burner always remains warm enough.

When burning-naphtha can be sold in quantity, it is advisable to mix it with *petroleum spirit*, which in this case is an improvement, and especially tends to keep it colourless. The petroleum spirit can be pumped into the still after the solvent naphtha has come over, and can be distilled along with the burning-naphtha. Care should be taken that about equal parts of coal-naphtha and petroleum spirit distil together; the smell of the latter will then not be perceptible. Or else the petroleum spirit is mixed with the naphtha after distillation. The best descriptions of petroleum spirit for this purpose are those which give off very little below 100°, but nearly the whole up to 170°.

We conclude with a *synoptical table of the distillation of coal-tar*, which is to represent one of the modes in which this manufacture may be carried on; but it is hardly necessary to say that the author does not mean to lay it down as the best in all cases, the preceding treatise offering many equally acceptable deviations in particular instances.

SYNOPSIS OF THE DISTILLATION OF COAL-TAR.

[The numbers in brackets denote the pages of this treatise where the operations referred to are described in detail.]

- DEHYDRATION, *a.* by standing [89]
 b. during the heating-up [91]..... } AMMONIACAL LIQUR.
- DISTILLATION.
- I. Fraction, up to 170° { Ammoniacal liquor
 First runnings [113, 251],
 rectified [262], yield:—
1. Product up to 110°, chemically washed [252],
 distilled by steam [265] yields *a* } 90-PER-CENT. BENZOL.
 b. Weaker benzol, goes to I. 2.
 2. Product up to 140°, treated like 1, yields *a* ... } 50-PER-CENT. BENZOL.
 b.
 c. Intermediate fraction, is redistilled.
 d. } SOLVENT NAPHTHA.
 3. Product up to 170°, treated like 1 and 2, yields *a* } BURNING-NAPHTHA.
 b.
 c. Residue, goes to II.
- II. Fraction, from 170° to 230°. Middle oil [117].
 Washed with caustic soda, yields:—
1. Oil, distilled in the light-oil still, yields
 a. Distillate up to 170°, goes to I. 3.
 b. " " 230°, yields [236]..... NAPHTHALENE.
 c. Residue, goes to III.
2. Alkaline liquor, decomposed by carbonic acid
 [220], yields:—
 a. Aqueous solution of sodium carbonate, caustic-
 ized by lime and used over again.
 b. Crude carbolic acid, is purified [224] and
 yields *a* CARBOLIC ACID.
 β. Waste oils, go back to II.
- III. Fraction, from 230° to 270° = Heavy oil [collected
 till solid matters begin to crystallize, pp. 121, 188].
 Can be treated for naphthalene [236], usually only
 employed as } CREOSOTE OIL
 Or else separated [121] into *a* }
 b. LUBRICATING-OIL.
- IV. Fraction, Anthracene oil [164].
 Filtered, or cold-pressed [166], yields:—
1. Oils, are redistilled and yield [174]
 a. Solid distillate, treated along with IV. 2;
 b. Liquid distillate, goes to III. *b.* or is redistilled;
 c. Residue (pitch, coke, &c.),

2. Residue, is hot-pressed [168] and yields

a. Oils, treated like IV. 1;

b. Crude anthracene, washed with naphtha &c.

[170] yields

a. ANTHRACENE.

β. Solution, is distilled and yields

aa. Naphtha, used over again for washing;

bb. Phenanthrene &c. is burnt to [80] LAMPBLACK.

V. *Pitch* [143]. Employed for patent fuel [150] or

varnishes &c. [152] PITCH.

Or else distilled [155], yielding:—

1. Crude anthracene, treated like IV. 2;

2. Lubricating-oil, goes to III. a, resp. III. b;

3. Residue [161] COKE.

CHAPTER XI.

AMMONIACAL LIQUOR.

THE ammoniacal liquor, or gas-liquor, is obtained at the gas-works partly by condensation in the hydraulic main and the condenser, along with the tar, and partly by washing the gas in the scrubbers. That from the hydraulic main is poorer than that from the condenser and the scrubbers. The total yield of ammoniacal liquor from the coals has been stated, pp. 13 & 14.

Some ammoniacal liquor is also obtained in distilling the tar, but solit tle (compare pp. 136 et seq.) that tar-distillers on a small scale, who have not at the same time contracts for gas-liquor, usually let that made by themselves run to waste.

The following Table (communicated to the author by Dr. C. Meymott Tidy) shows how little the nitrogen of the coals is utilized in this respect:—

Origin of the coal.	Percentage of nitrogen.	Possible yield of NH_3 , per cent.	Possible yield of ammoniacal liquor, 4° Tw., per ton of coals, gallons.
Wales	0.91	1.10	142
Lancashire	1.25	1.52	196
Newcastle	1.32	1.60	206
Scotland.....	1.44	1.75	226

Instead of this *possible* yield, rarely more than 45 gallons of gas-liquor of 4° Tw. is obtained per ton of coals, usually only 25, in London only 13 gallons.

From this source, the dry distillation of coal, is derived most, by

x 2

far, of the ammonia and its salts consumed in the arts. That obtained in the manufacture of bone-charcoal, prussiate of potash, manure, &c. does not, comparatively, amount to much. But we have seen (p. 14) that for ammonia as well as for tar a new and abundant source of supply would be opened up if the coking of coals could be carried out with recovery of those by-products; and this seems to be only a question of time.

The consumption of ammonia has increased enormously, especially during the last twenty years, first and foremost for manure, and in a secondary degree by the introduction of the manufacture of soda ash by the ammoniacal process*. Principally owing to the constantly increasing demand for sulphate of ammonia as manure, the price of all ammonia compounds has doubled within that period; neither has it been possible, in spite of that, to replace ammonia by sodium nitrate, more especially for the culture of beetroot for sugar. This enormous rise of price has naturally called forth numerous attempts to produce ammonia in other ways and from all possible sources, especially from the nitrogen of the atmosphere. Those attempts have not yet led to any tangible results; and certainly no ammonia thus produced is an article of commerce. In this treatise we shall only describe the working-up of the ammoniacal liquor of gas-works; but the same description will apply to the similar liquors from the manufacture of bone-charcoal and prussiate of potash.

Components of Ammoniacal Liquor.

Gas-liquor is an aqueous solution (holding a little tar in mechanical suspension) of the following substances, together with very small quantities of others:—

Free ammonia †,
Ammonium carbonates,
Ammonium sulphide,
Ammonium sulphocyanide,
Ammonium acetate,

* Compare Lunge, 'Manufacture of Sulphuric Acid and Alkali,' Van Voorst, 1880, vol. iii. p. 1.

† Occurs in gas-liquor according to Gerlach and Tiefttrunck (Wagner's Jahresh. 1877, p. 1035).

Ammonium chloride,
 Ammonium sulphate,
 Ammonium sulphite (?),
 Ammonium thiosulphate (hyposulphite),
 Salts of organic nitrogenized bases.

The following table (by Gerlach) of the composition of some gas-liquors possesses merely a comparative value, as, for instance, ammonium sulphocyanide is not mentioned at all.

1 litre of gas-liquor contains (in grams) :—

	Chemnitz gas-works. Zwickau coal.	Saxon town. Zwickau coal.	Bonn gas-works. Ruhr coal.	Treves gas-works. Saar coal.	Zurich. Saar coal.
Total ammonia	12.090	9.40	18.12	15.23	3.47
Ammonium thiosulphate.....	1.036	1.628	5.032	2.072	0.296
" sulphide	0.340	0.646	6.222	2.468	1.428
" bicarbonate	1.050	1.470	2.450	33.763	5.856
" monocarbonate .	4.560	7.680	33.120		
" sulphate	0.462	0.858	1.320		
" chloride	30.495	17.120	3.745	4.922	1.926
" salts, total	37.943	29.402	51.889	49.225	9.506

This shows very great differences, both in the total ammonia and in its distribution among the several salts, between the different liquors.

The following table (p. 310) by Gerlach, comprises the results of his own and other tests for total ammonia in sundry gas-liquors.

PROPERTIES OF THE COMPONENTS OF GAS-WATER.

Ammonia, NH_3 .

Colourless gas, of pungent smell and sharp alkaline taste. Common ammonia, from its admixture of organic bases, has a much more disagreeable smell than pure. Spec. grav. 0.5967; 1 litre at 0° and 0.76 metre pressure weighs 0.7635 gram; vapour-

Coal distilled.	Grams NH ₃ per 100 c. c.	Degrees Baumé.	Gas-works.
<i>German Coals.</i>			
Zwickau coal.....	1·209	1·6	Ohemnitz.
" and Bohemian lig- nite.....	0·908	1·66	Leipzig.
Zwickau and Burgk coal ...	0·944	1·5	Dresden.
Burgk coal.....	1·862	2·8	Freiberg.
Buhr coal	1·812	2·1	Bonn.
" "	1·292	1·75	Rupen.
" "	1·826	2·25	Cologne.
" "	1·278	1·5	Dortmund.
Saar coal	1·574	...	Augsburg.
" "	1·523	2·5	Treves.
" "	1·870	3·2	Zurich.
" "	1·435	3	Munich.
Silesian coal	2·339	3	Berlin.
" "	1·290	...	Pest.
" and Bohemian lig- nite.....	1·030	2	Prague.
<i>English Coals.</i>			
Cannel coal; boghead	2·881	3·75	Hamburg.
English coal	3·514	4	Stettin.
" "	2·659	3	St. Petersburg.
" "	2·244	3·3	Trieste.
" "	2·142	3·5	Stralsund.
Leverson Wallsend; Old Pelton Main	2·366	4	Altona.
English coal	2·407	4	Copenhagen.
New Pelton; Ravensworth	1·785	2·75	Riga.
Old Pelton Main	1·717	3	Königsberg.
English coal	2·966	3	Stettin.
Old Pelton Main; Leverson Wallsend	1·345	3	Dantzic.

tension at 0° = 4·8 atmospheres*. Can be condensed by pressure and cold to a very mobile, colourless and strongly refringent liquid of sp. gr. 0·6362 at 0°.

Composition: 82·39 per cent. N, 17·61 per cent. H.

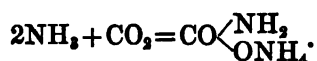
By a strong red heat it is decomposed, but very slowly, especially when mixed with other gases. With red-hot coal it gives ammonium cyanide and hydrogen:



(This condition is always present in gas-retorts.) Solutions of

* The vapour-tension of ammonia between -34·7° and +20° has been determined by Bunsen, Poggend. Annal. xlv. p. 95.

alkaline hypobromites expel all the nitrogen from ammonia and its salts. (Upon this fact is based the azotometer, proposed by Knop for estimating ammonia.) With dry carbon dioxide, dry NH_3 yields ammonium carbamate :



If moisture be present, ammonium carbonate is also formed.

Ammonia is absorbed with avidity by water. 1 gram of water at 0° and 0.76 metre pressure absorbs * 1146 c. c. of ammonia-gas = 0.899 gram NH_3 , at 10° only 0.679 gram, at 20° 0.526 gram, at 30° 0.403 gram, at 100° 0.074 gram. (Exact statements on the influence of pressure and temperature upon the solubility of ammonia in water are given by Roscoe & Dittmar, *loco citato*, and by Sims, Ann. Chem. Pharm. cxviii. p. 345.)

Of the tables of specific gravity of aqueous ammonia we shall first give that by Carius, for the temperature of 14° .

NH_3 .	Spec. grav.	NH_3 .	Spec. grav.	NH_3 .	Spec. grav.
per cent.		per cent.		per cent.	
36.0	0.8844	30.6	0.8962	25.2	0.9100
35.8	0.8848	30.4	0.8967	25.0	0.9106
35.6	0.8852	30.2	0.8971	24.8	0.9111
35.4	0.8856	30.0	0.8976	24.6	0.9116
35.2	0.8860	29.8	0.8981	24.4	0.9122
35.0	0.8864	29.6	0.8986	24.2	0.9127
34.8	0.8868	29.4	0.8991	24.0	0.9133
34.6	0.8872	29.2	0.8996	23.8	0.9139
34.4	0.8877	29.0	0.9001	23.6	0.9145
34.2	0.8881	28.8	0.9006	23.4	0.9150
34.0	0.8885	28.6	0.9011	23.2	0.9156
33.8	0.8889	28.4	0.9016	23.0	0.9162
33.6	0.8894	28.2	0.9021	22.8	0.9168
33.4	0.8898	28.0	0.9026	22.6	0.9174
33.2	0.8903	27.8	0.9031	22.4	0.9180
33.0	0.8907	27.6	0.9036	22.2	0.9185
32.8	0.8911	27.4	0.9041	22.0	0.9191
32.6	0.8916	27.2	0.9047	21.8	0.9197
32.4	0.8920	27.0	0.9052	21.6	0.9203
32.2	0.8925	26.8	0.9057	21.4	0.9209
32.0	0.8929	26.6	0.9063	21.2	0.9215
31.8	0.8934	26.4	0.9068	21.0	0.9221
31.6	0.8938	26.2	0.9073	20.8	0.9227
31.4	0.8943	26.0	0.9078	20.6	0.9233
31.2	0.8948	25.8	0.9083	20.4	0.9239
31.0	0.8953	25.6	0.9088	20.2	0.9245
30.8	0.8957	25.4	0.9094	20.0	0.9251

* Roscoe & Dittmar, Ann. Chem. Pharm. cxii. p. 349.

Table (continued).

NH ₃ .	Spec. grav.	NH ₃ .	Spec. grav.	NH ₃ .	Spec. grav.
per cent.		per cent.		per cent.	
19.8	0.9257	13.2	0.9477	6.6	0.9725
19.6	0.9264	13.0	0.9484	6.4	0.9733
19.4	0.9271	12.8	0.9491	6.2	0.9741
19.2	0.9277	12.6	0.9498	6.0	0.9749
19.0	0.9283	12.4	0.9505	5.8	0.9757
18.8	0.9289	12.2	0.9512	5.6	0.9765
18.6	0.9296	12.0	0.9520	5.4	0.9773
18.4	0.9302	11.8	0.9527	5.2	0.9781
18.2	0.9308	11.6	0.9534	5.0	0.9790
18.0	0.9314	11.4	0.9542	4.8	0.9799
17.8	0.9321	11.2	0.9549	4.6	0.9807
17.6	0.9327	11.0	0.9555	4.4	0.9815
17.4	0.9333	10.8	0.9563	4.2	0.9823
17.2	0.9340	10.6	0.9571	4.0	0.9831
17.0	0.9347	10.4	0.9578	3.8	0.9839
16.8	0.9353	10.2	0.9586	3.6	0.9847
16.6	0.9360	10.0	0.9593	3.4	0.9855
16.4	0.9366	9.8	0.9601	3.2	0.9863
16.2	0.9373	9.6	0.9608	3.0	0.9873
16.0	0.9380	9.4	0.9616	2.8	0.9882
15.8	0.9386	9.2	0.9623	2.6	0.9890
15.6	0.9393	9.0	0.9631	2.4	0.9899
15.4	0.9400	8.8	0.9639	2.2	0.9907
15.2	0.9407	8.6	0.9647	2.0	0.9915
15.0	0.9414	8.4	0.9654	1.8	0.9924
14.8	0.9420	8.2	0.9662	1.6	0.9932
14.6	0.9427	8.0	0.9670	1.4	0.9941
14.4	0.9434	7.8	0.9677	1.2	0.9950
14.2	0.9441	7.6	0.9685	1.0	0.9959
14.0	0.9449	7.4	0.9693	0.8	0.9967
13.8	0.9456	7.2	0.9701	0.6	0.9975
13.6	0.9463	7.0	0.9709	0.4	0.9983
13.4	0.9470	6.8	0.9717	0.2	0.9991

The following table by Wachsmuth (Wagner's Jahresb. 1876, p. 447) refers to a temperature of 12° C.

Specific gravity at 12°.	1 kilog. con- tains of NH ₃	1 litre con- tains of NH ₃	1 litre consists of	
			water.	liquid ammonia.
	grams.	grams.	cub. centim.	cub. centim.
0.870	384.4	334.5	535.5	464.5
0.872	376.9	328.6	543.4	456.6
0.874	369.4	322.8	551.2	448.8
0.876	362.0	317.1	558.9	441.1
0.878	354.6	311.3	566.7	433.3
0.880	347.2	305.5	574.5	425.5
0.882	340.0	299.8	582.2	417.8
0.884	332.9	294.2	589.8	410.2

Table (continued).

Specific gravity at 12°.	1 kilog. con- tains of NH_3	1 litre con- tains of NH_3	1 litre consists of	
			water.	liquid ammonia.
	grams.	grams.	cub. centim.	cub. centim.
0.886	325.8	288.6	597.4	402.6
0.888	318.7	283.0	605.0	395.0
0.890	311.6	277.3	612.7	387.3
0.892	304.7	271.7	620.3	379.7
0.894	297.8	266.2	627.8	372.2
0.896	290.9	260.6	635.4	364.6
0.898	284.1	255.1	642.9	357.1
0.900	277.3	249.5	650.5	349.5
0.902	270.7	244.1	657.9	342.1
0.904	264.1	238.7	665.3	334.7
0.906	257.7	233.4	672.6	327.4
0.908	251.3	228.2	679.8	320.2
0.910	244.9	222.8	687.2	312.8
0.912	238.6	217.6	694.4	305.6
0.914	232.3	212.3	701.7	298.3
0.916	226.0	207.0	709.0	291.0
0.918	219.7	201.6	716.4	283.6
0.920	213.4	196.3	723.7	276.3
0.922	207.3	191.1	730.9	269.1
0.924	201.2	185.9	738.1	261.9
0.926	195.1	180.6	745.4	254.6
0.928	189.0	175.4	752.6	247.4
0.930	182.9	170.1	759.9	240.1
0.932	176.9	164.8	767.2	232.8
0.934	170.9	159.6	774.4	225.6
0.936	164.9	154.3	781.7	218.3
0.938	158.9	149.0	789.0	211.0
0.940	152.9	143.7	796.3	203.7
0.942	147.1	138.5	803.5	196.5
0.944	141.3	133.3	810.7	189.3
0.946	135.6	128.2	817.8	182.2
0.948	129.9	123.1	824.9	175.1
0.950	124.2	118.0	832.0	168.0
0.952	118.7	113.0	839.0	161.0
0.954	113.2	108.0	846.0	154.0
0.956	107.8	103.0	853.0	147.0
0.958	102.4	98.1	859.9	140.1
0.960	97.0	93.1	866.9	133.1
0.962	91.6	88.1	873.9	126.1
0.964	86.2	83.0	881.0	119.0
0.966	80.8	78.0	888.0	112.0
0.968	75.5	73.0	895.0	105.0
0.970	70.2	68.0	902.0	98.0
0.972	65.2	63.6	908.7	91.3
0.974	60.2	58.6	915.4	84.6
0.976	55.2	53.8	922.2	77.8
0.978	50.2	49.1	928.9	71.1
0.980	45.3	44.3	935.7	64.3
0.982	40.4	39.6	942.4	57.6
0.984	35.5	34.9	949.1	50.9
0.986	30.6	30.1	955.9	44.1
0.988	25.8	25.5	962.5	37.5
0.990	21.0	20.7	969.3	30.7

Ammonium Carbonate.

Several of the compounds of carbonic acid and ammonia, formerly assumed to be present, are not acknowledged now; and only those mentioned below are so. They are all decomposed at a red heat into carbon dioxide, ammonia, and water respectively; hence they do not exist as compounds in the gas while hot, but are only formed on its cooling, probably partly in the condensation of an aqueous solution.

Neutral salt $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Lengthened plates; smells and tastes like ammonia; effloresces in the air with formation of acid salt, losing ammonia and water; splits up at 58° into water, carbon dioxide, and ammonia. When it is dissolved in water, it can be recrystallized unchanged by cooling; but the dilute aqueous solution already contains a mixture of free ammonia and neutral and acid ammonium carbonate. The aqueous solution begins to give off gas at 70° or 75° , boils at 75° or 80° , and gives off CO_2 and NH_3 in the same proportion as they exist in the salt.

Semiacid salt, $(\text{NH}_4)_4\text{H}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$. Thin hexagonal plates; smell and taste of ammonia. Decomposed by a little water; dissolves unchanged in 5 parts of water at 15° , which solution rapidly evolves gas when heated.

Acid salt, $(\text{NH}_4)\text{H}(\text{CO}_3)$ = ammonium bicarbonate. Is found ready formed in many guano beds &c., also frequently in gas-purifiers, pipes, &c. This salt is usually assumed to exist in gas-liquor; but some assert that the other carbonates occur there as well. It is always formed when the other salts richer in ammonia or ammonium carbamate effloresce. It occurs as a white mealy powder or as rhombic crystals, mostly columnar. Sp. gr. 1.573 (Schiff); the natural one = 1.45 (Ulex). In the dry state it does not smell of ammonia; it tastes cooling and saline. In dry air it is stable; in moist air the crystals lose their brilliancy. At 60° it slowly decomposes into CO_2 , NH_3 , and H_2O . It readily dissolves in water; in the air the solution rapidly loses carbonic acid, and on being gently heated gives off gas-bubbles, a salt richer in ammonia remaining behind. According to Dibbits*, 100 parts of water dissolve

At 0°	10°	15°	20°	25°	30°
11.9	15.8	18.3	21.0	23.9	27.0 parts of salt.

* Dangler's Journal, ccxvi. p. 164.

Ammonium carbamate (formerly called dry ammonium carbonate), $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{ONH}_4 \end{smallmatrix}$, hence forming the intermediate term between neutral ammonium carbonate, $\text{CO} \begin{smallmatrix} \text{ONH}_4 \\ \diagdown \\ \text{ONH}_4 \end{smallmatrix}$, and carbamide or urea, $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{NH}_2 \end{smallmatrix}$. It is always formed when ammonia and carbon dioxide

meet nearly in the dry state and not too hot, and even in the presence of moisture if at least 2 vols. NH_3 are present to 1 vol. CO_2 ; hence it is a principal component of commercial ammonium carbonate, and can be obtained from this by slow distillation &c. It occurs in large plates or crystalline crusts, smells strongly of ammonia, deliquesces in the air, and almost completely volatilizes. At 59° or 60° it decomposes entirely into CO_2 and 2NH_3 ; at 50° or 55° it is re-formed from these components. It dissolves in $1\frac{1}{2}$ part of water with considerable absorption of heat, and is then quickly converted into the acid salt, ammonia being given off.

Commercial carbonate of ammonia, salt of hartshorn, sal volatile, is a mixture of ammonium bicarbonate and ammonium carbamate, usually containing a little adhering water. It is formed from a mixture of carbon dioxide (even in excess) and ammonia gas in the presence of sufficient aqueous vapour, consequently also in the quick distillation of any of the ammonium carbonates, or of ammonium chloride or sulphate with chalk; in all these cases no doubt CO_2 , NH_3 , and H_2O must be assumed to exist free while in the state of vapour. Formerly the commercial salt had the formula



when gently heated in a retort it gradually liquefied, and dissolved

At 13°	$16^\circ.7$	32°	$40^\circ.6$	49°
In 4	3.3	2.7	2.4	2 parts of water.

The salt now manufactured is richer in ammonia, according to the formula



It remains solid on heating; in the air it effloresces, losing 47 per cent. by weight, and leaving friable ammonium bicarbonate behind. The same is left when the salt is treated with a small quantity of water.

It dissolves at 15° in 4 parts of water, with considerable absorption of heat, at 65° in $1\frac{1}{2}$ part. At 75° the solution begins to give

off much CO_2 , at 85° also ammonia; at 100° all the salt is volatilized. In dilute solutions the liberation of the salt takes place later on.

Vogler * considers commercial carbonate of ammonia to be a compound of neutral ammonium carbonate with ammonium carbamate.

Ammonium sulphide.

There exist a monosulphide, $(\text{NH}_4)_2\text{S}$, a sulphhydrate, NH_4SH , and several polysulphides, containing from 2 to 7 atoms of S to 2 molecules of NH_4 . They are all volatile, soluble in water, and easily decomposable.

Ammonium monosulphide, $(\text{NH}_4)_2\text{S}$, is formed from hydrogen sulphide and ammonia in excess. At -18° colourless shining crystals, dissolving readily and without colour in water. This solution is stable, whilst the crystals in the air at once lose half their ammonia. In the state of vapour it cannot exist, but dissociates into NH_3 and H_2S .

Ammonium sulphhydrate, NH_4SH , is formed by passing hydrogen sulphide into liquor ammoniæ to saturation (the ordinary laboratory reagent). The originally colourless solution soon turns yellow in the air, polysulphides being formed. Below -10° it can be crystallized; on evaporation it dissociates into H_2S and NH_3 . On prolonged contact with air the solution deposits sulphur, and ammonium thiosulphate is formed.

The polysulphides are also prepared by dissolving sulphur in ordinary ammonium sulphide.

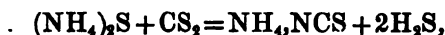
Ammonium sulphide has not hitherto been manufactured on a large scale; but this might be done, according to Spence, by mixing in a retort sulphate of ammonia with alkali waste or spent gas-lime (both of them very rich in calcium sulphide), blowing in steam, and passing the vapours into a condensing-apparatus. Care must, however, be taken lest the pipes be stopped up by solidifying ammonium sulphide.

Ammonium sulphocyanide, NH_4CNS .

Colourless shining scales, without water of crystallization; that crystallized from an aqueous solution is somewhat deliquescent; that from alcohol is stable in the air. Very soluble in water, with considerable lowering of the temperature, and in alcohol.

* Zeitschr. für anal. Chemie, xvii. p. 451.

On heating the dry salt it fuses at 145–160°, and decomposes soon after. Consequently it cannot exist in the state of vapour, but is only formed on cooling from ammonium sulphide and carbon bisulphide,



or else from ammonium cyanide and sulphide. In English gas-liquors from 3 to 5 ounces of ammonium sulphocyanide per gallon is found. It is also found in considerable quantities in the spent oxide of iron of the gas-purifiers.

Ammonium cyanide, NH_4CN .

A colourless salt, crystallizing in cubes, smelling and tasting both of prussic acid and ammonia, with an alkaline reaction, as poisonous as prussic acid. It is very soluble in water and alcohol; it is very volatile, boiling, according to some chemists, at 36°; but, from its vapour-density, it must be assumed to undergo dissociation into ammonia and prussic acid. The dry salt is very unstable, and in the air is quickly converted into a brown nitrogenous substance (azulmic acid).

Ammonium chloride (Sal-ammoniac), NH_4Cl .

Known from ancient times; also ready formed in nature. In the pure state without colour or taste. Crystallizes from water or alcohol in octahedra arranged in the form of feathers, from urea in cubes. Sublimed sal-ammoniac consists of fritted fibrous crystalline masses. It is very tough and difficult to powder. Sp. gr. 1.52. Soluble in water with much absorption of heat. 100 parts of water dissolve

At 0°	10°	110°
28.4	32.8	77.2 parts.

Specific gravity of Solutions of Ammonium Chloride at 15°.

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1.00316	10	1.03081	19	1.05648
2	1.00632	11	1.03370	20	1.05929
3	1.00948	12	1.03658	21	1.06204
4	1.01264	13	1.03947	22	1.06479
5	1.01580	14	1.04325	23	1.06754
6	1.01880	15	1.04524	24	1.07029
7	1.02180	16	1.04804	25	1.07304
8	1.02481	17	1.05086	26	1.07375
9	1.02781	18	1.05367		

Ammonium chloride is not volatile at the ordinary temperature. On being heated it evaporates without fusing, and sublimes in crusts (as above mentioned). Its vapour is a dissociated mixture of NH_3 and HCl . On boiling its aqueous solution a little ammonia escapes, and the reaction becomes distinctly acid; hence it strongly acts upon metal (especially iron) vessels, and is contaminated itself. Even in the neutral state ammonium chloride in the presence of water acts strongly upon iron, copper, &c., and promotes the corrosion of these metals.

Ammonium Sulphate.

Of the different sulphates of ammonia we are only interested in the *neutral*, $(\text{NH}_4)_2\text{SO}_4$, which occurs in transparent rhombic crystals, isomorphous with potassium sulphate. Sp. gr. 1.76; bitter, acrid taste; decrepitates on being heated, fuses at 140° , and begins to decompose at 280° ; it cannot be volatilized without change. 100 parts of water dissolve at

0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
71.0	73.65	76.3	78.95	81.6	84.25	86.9	89.55	92.2	93.85	97.5

parts of the salt. In absolute alcohol it is insoluble.

Specific gravity of the Solutions of Ammonium Sulphate at 15°C .

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1.0057	18	1.1035	35	1.2004
2	1.0112	19	1.1092	36	1.2060
3	1.0172	20	1.1149	37	1.2116
4	1.0230	21	1.1207	38	1.2172
5	1.0287	22	1.1265	39	1.2228
6	1.0345	23	1.1323	40	1.2284
7	1.0403	24	1.1381	41	1.2343
8	1.0460	25	1.1439	42	1.2402
9	1.0518	26	1.1496	43	1.2462
10	1.0575	27	1.1554	44	1.2522
11	1.0632	28	1.1612	45	1.2583
12	1.0690	29	1.1670	46	1.2644
13	1.0747	30	1.1724	47	1.2705
14	1.0805	31	1.1780	48	1.2766
15	1.0862	32	1.1836	49	1.2828
16	1.0920	33	1.1892	50	1.2890
17	1.0977	34	1.1948		

VALUATION OF AMMONIACAL LIQUOR.

This is frequently done at the gas- and tar-works by means of the hydrometer, for the sake of convenience. But this process is most deceptive; for the ammonium salts raise the density of the solution in an unequal degree, and free ammonia (which, however, does not frequently occur) even lowers it. The following table, by Seidel*, proves how unequal are the percentages of ammonia in different gas-liquors of the same specific gravity (at 15°).

Degrees Baumé...	2°	2°·5	3°	3°·5	4°	4°·5	5°	6°
Specific gravity...	1·0188	1·0163	1·0208	1·0249	1·0280	1·0316	1·0352	1·0426
Per cent. NH ₃ ...	1·16 1·42 1·50 1·77	1·30 1·43 1·63 1·77 1·98 2·18 2·65	1·63 1·76 1·90 2·10 2·38 2·45	1·87 2·00 2·24 2·40 2·72	2·55 2·72 2·90 3·40	2·79 2·85 3·06 3·40 3·53	3·67	3·74

Similar observations have been made by T. H. Davis †.

It is consequently decidedly preferable to value gas-liquor by a chemical test. Usually only the volatile ammonium salts are estimated, the ammonia of which is given off on distillation without lime, and is indicated by titrating with sulphuric acid without heating. The ammonium salts with stronger acids, *i. e.* the sulphate, chloride, and sulphocyanide, can be all the more left out of account, as the ammonia thus present hardly ever amounts to more than 0·3 per cent.

The most rational way (which is also the usual one in Germany) is, to employ the ordinary standard acid, which contains 0·049 gram SO₄H₂ per cubic centimetre, and indicates 0·017 gram NH₃. When litmus is employed, a certain volume of gas-liquor, say 20 c. c., should be first supersaturated with standard acid (for which

* Hofmann's Bericht über die Wiener Ausstellung, i. p. 194.

† Chem. News, xxxviii. p. 193

purpose 40 c.c. will suffice in most cases), and boiled to expel all carbon dioxide and hydrogen sulphide; and then the litmus solution is added and the excess of acid retitrated by standard alkali (soda or seminormal ammonia). In direct titration with acid a solution of litmus cannot be very well employed, because it is discoloured by sulphuretted hydrogen; in this case litmus paper can be employed, which, after a little practice, does not take much time; or else some of the azo-colours are employed, which permit exact working in the cold and are not affected either by CO_2 or H_2S . The best of these are the dimethylaniline-orange, or an alcoholic solution of amido-azobenzene*.

In England it is usual to prepare a standard acid by diluting 1 lb. of rectified oil of vitriol to a gallon; the specific gravity of the dilute acid ought to be $= 1.068$ †. Of the gas-liquor 16 liquid-ounces are measured off; and the acid is run in, from a measure graduated to liquid-ounces, till the litmus paper indicates neutrality. The number of the measures of acid consumed indicates the number of ounces of concentrated oil of vitriol which each gallon of the gas-liquor requires for saturation. The rule is that each degree Twaddle corresponds to about two ounces of sulphuric acid; *e. g.* gas-liquor of 4° Tw. will saturate 8 ounces. But this is any thing but correct; usually less acid is required than, according to the hydrometer, should be expected. But even the acid test, as carried out in England, is very incorrect; for "rectified oil of vitriol" may contain from 92 to 96 per cent. of SO_4H_2 . Usually it is 93 per cent., in which case each liquid-ounce of the test acid answers to 0.323 ounce of NH_3 per gallon of the gas-liquor, or 0.202 part NH_3 by weight in 100 parts gas-liquor by volume.

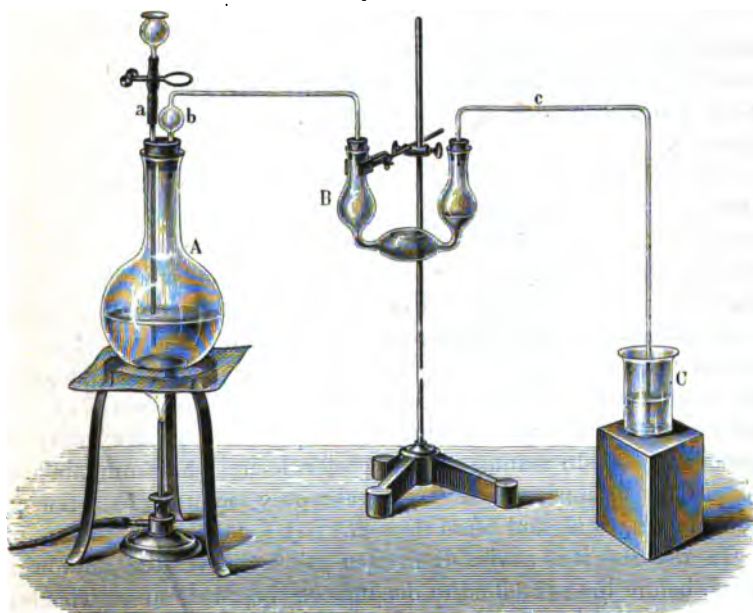
If the total ammonia, including that combined with strong acids, has to be estimated, the gas-liquor is distilled with alkali, lime, or baryta, and the vapours are received either into water or, better, at once into standard sulphuric acid, the unsaturated acid being afterwards determined by standard alkali, (compare conclusion of this chapter). Some prefer lime or baryta to the alkalies, on the (unfounded) assumption that the former are better, not splitting up organic alkaloids, while equally producing ammonia; on the contrary, lime is less convenient than alkali, owing to the bumping

* These dyes are to be obtained from most dealers in coal-tar colours; compare the author's observations and special directions, *Chemical News*, vol. xliv. p. 288.

† This is not correct; ordinary "rectified oil of vitriol" at 15° will only give 1.060.

of the liquid, which can only be prevented by continually aspirating a slight current of air through it. It is better to employ caustic soda for decomposing the ammonia salts, and to distil the liquid almost to dryness, so as to make sure of driving over all the ammonia. The apparatus represented in fig. 71 serves for this purpose. A is a flask, provided with a funnel pipe closed by a pinch-cock, for running in the caustic-soda solution; *b* is the gas-delivery

Fig. 71.



pipe, provided with a bulb, and cut off obliquely below, connected with the receiver B. The latter is connected with the safety-tube *c*, dipping into the beaker C, to prevent accidental loss by spurting over of standard acid.

THE WORKING-UP OF AMMONIACAL LIQUOR.

Formerly so much of the gas-liquor as was not let run to waste used to be saturated directly with sulphuric acid, and the solution evaporated till the ammonium sulphate crystallized out. The gases escaping at the saturation, carbon dioxide and hydrogen sulphide,

were sometimes passed through a fire to burn the latter gas—which was done very incompletely, owing to the admixed moisture and carbon dioxide. The resulting sulphate of ammonia was very much discoloured by tarry substances, and would nowadays be hardly saleable. Direct saturation must be pronounced to be irrational, even for this reason—that the evaporation of such dilute solutions takes more fuel than the driving off of ammonia in properly constructed apparatus. Probably the former process is but rarely employed now.

Far preferable is volatilization of the ammonia from the gas-liquor, and its absorption in sulphuric acid. This can be done in various ways, of which we shall first give a brief general description, to be followed by descriptions of a number of practically tried apparatus.

First of all, the question is whether *lime* is to be used in the distillation or not. Most of the ammonia in gas-liquor is present in the form of salts which volatilize on boiling, although with dissociation—essentially ammonium carbonate and sulphide. These can be expelled by boiling without lime. But ammonium sulphate, chloride, and sulphocyanide remain behind on boiling, and may be called “fixed” under these circumstances. If the ammonia of these salts is to be obtained, it must be expelled by means of lime, which complicates the apparatus and process. Hence many, especially English, manufacturers prefer losing the ammonia only obtainable by lime, which in any case only amounts to a few per cent. of the total, and often does not pay for recovering.

In any case it is advisable first to expel the volatile ammonium salts, before lime is added to decompose the fixed ones. This both saves lime and lessens the inconvenience connected with its use. The escape of hydrogen sulphide cannot be avoided even by a great excess of lime, as calcium sulphide is decomposed by boiling with water; and the residual calcium sulphide is itself a nuisance.

It is very important to provide with *safety-valves* all stills intended for expelling ammonia salts without lime. Otherwise the gas-delivery pipes easily get plugged up by ammonium carbonate, which may lead to dangerous explosions*; such danger is entirely avoided by fitting up the boilers with safety-valves.

The apparatus, moreover, essentially differ in the way in which

* Compare Seidel in Hofmann's Wiener Ausstellungs-Bericht, vol. i. p. 196. Watson Smith (private communication) has also observed this.

the ammonia is expelled, and the agents employed for this purpose—direct fire, open steam, indirect steam. Expelling the ammonia by boiling alone, without employing the sensible and latent heat of the vapours, consumes very much time and fuel; the additional first cost of a properly constructed apparatus, in which the heat alluded to is utilized for a preliminary heating of fresh gas-liquor, and the gas is freed from aqueous vapour by dephlegmation, is soon paid for by an enormous saving in fuel. In the special descriptions to be given afterwards the apparatus now usually employed for this purpose will be explained in detail; their principle is the same as that carried out in rectifying spirit of wine, or light tar-oils (p. 277 *et seq.*); but the details must necessarily differ.

Which kind of heating is most advantageous for distilling ammonia, seems to be decided by the following experiments on a manufacturing-scale, made by Dr. C. M. Tidy. A quantity of gas-liquor amounting to 7000 gallons required

	hours.	Yield, as compared with the theory.
when heated by open fire from without.....	22	90 per cent.
when heated by a steam-coil (indirect steam)	18	92 „
when open steam was blown in	14	98.5 „

A further difference is caused by the fact that sometimes the gas-liquor is worked at once for *liquor ammoniæ*, whilst mostly sulphate of ammonium is aimed at. In the former case sufficient lime must be employed for retaining carbon dioxide and hydrogen sulphide as much as possible; but since certain complicated alkaloids of empyreumatic nature always occur in gas-liquor, the liquid ammonia made direct from this always retains a yellowish colour and a more or less tarry smell. These drawbacks may be obviated to a great extent by filtering the vapours through recently ignited wood charcoal. Some recommend, as more convenient, passing the vapours through a fatty oil, which retains the tarry substances and can be again [partially] freed from them by heating. Or else the liquor is redistilled with potassium permanganate, which also destroys the ammonium sulphide unavoidably present (compare p. 322).

Watson Smith * advises in any case, even when liquor ammoniæ is the principal product, making along with it a little sulphate,

* Private communication.

because the gas which first and somewhat tempestuously escapes in the distillation carries along with it some tarry matters and hence is best not employed for making liquor ammoniæ. This of course cannot be observed in the continuously acting apparatus to be described below; but even then only crude strong ammoniacal liquor is at first obtained, from which liquor ammoniæ is prepared by distilling into pure water. In order to carry off separately the first evolved portion of ammoniacal gas, the gas-delivery pipe of the ammonia-still is provided with two branches, each of them to be shut off by a stop-cock, or by a short piece of two-inch india-rubber pipe with a screw clamp, in order to direct the vapours either into the ordinary saturating-vessel filled with sulphuric acid, or into a worm for condensing crude liquor ammoniæ. The latter is collected in large iron tanks, from which the vapours pass first through a barrel half filled with water, or preferably, to avoid pressure, through a lead worm, serving as a reflux condenser, in which the vapours ascend and are met by water trickling down from a funnel, to condense the last traces of ammonia. (No doubt a small coke scrubber, fed with water or preferably with sulphuric acid, would act even more thoroughly.) Later on we shall describe the apparatus in which this crude liquor is treated in order to prepare pure liquor ammoniæ.

If *sulphate of ammonia* is worked for, there are two different systems of absorption, either of which may be employed. In one of them the gas, dehydrated by dephlegmation, is condensed in *dilute* sulphuric acid, so that no salt is separated during the saturation; the solution formed is clarified by repose, and is then evaporated (mostly in lead pans by means of a steam-coil) up to crystallization. The mother liquor is employed for diluting a fresh quantity of sulphuric acid. The other system consists in absorbing the ammonia vapours in *somewhat concentrated* sulphuric acid (say 140° Tw.), in which case the ammonium sulphate separates in the solid state in the saturating-vessels and is fished out from time to time. More acid is run in continuously, in a thin jet, so that the saturator is always kept filled up to the same level. The second process has the advantage of being continuous and saving all evaporation, but the drawback that the liquor cannot clarify and the salt does not come out so pure as in the first process.

Watson Smith* recommends the following plan for obtaining

* Private communication.

perfectly white sulphate. The saturator is charged with sulphuric acid diluted up to a suitable degree (say 80° Tw.), and ammonia is passed in until there is a slight smell of it. The excess is taken away by a little acid; and the separated sulphate is *at once* fished out, whereupon the operation can commence again. But if the acid is run in little by little and the gas passed through for a long time, the separating sulphate is black; and so it is in the former case, when the liquor has been proved by its smell to contain an excess of ammonia, if fresh acid is run in and fresh gas is passed through without fishing out the sulphate already formed, but allowing it to gradually accumulate. In fact the rule is, to fish out the *freshly-deposited* sulphate from *tolerably acid* mother liquors. The fishing is done by means of a ladle of galvanized iron perforated with numerous small holes; the sulphate is thrown upon a lead-lined drainer, from which the mother liquor runs back into the saturator.

In England, usually, sulphuric acid *made from brimstone* is employed in the manufacture of sulphate of ammonia, because pyrites acid contains iron and arsenic, both of which discolour the sulphate. F. C. Hills* avoids this by allowing the (pyrites) acid to meet with an excess of ammonia, which precipitates iron and arsenic (?); the excess is absorbed in another vessel, in the manner described in the patent. In Germany, pyrites acid is used; and the resulting sulphate has a grey tinge, but is as valuable for manure as the best white (and a great deal of such grey sulphate is sold in England also): but acid from Spanish pyrites (which is almost universal in England) is avoided, because its arsenic tinges the sulphate a greenish yellow.

A patent taken out by P. S. Brown (No. 804, Feb. 27, 1878) refers to employing iron concentrating-pans, the liquor being constantly kept slightly alkaline.

Sometimes the ammonia vapours are absorbed in hydrochloric acid, and *sal-ammoniac* is thus made. But this is only done exceptionally, both because that salt is not used any thing like so extensively as the sulphate, and because it cannot be obtained sufficiently pure in this way. Hot hydrochloric acid can only be kept in stone or earthenware vessels, which makes the apparatus both expensive and inconvenient; and the dense vapours of sal-ammoniac, which are unavoidable, are also very unpleasant.

On the other hand it is very rational to make *ammonium carbo-*

* Patent, No. 3257, Aug. 17, 1878.

nate by the direct plan of bringing together the ammonia vapours and carbonic acid, thus producing commercial carbonate of ammonia (p. 315). We shall revert to this process later on.

Lastly the apparatus differ according to whether they are adapted for *destroying the hydrogen sulphide* or not. Recently the sanitary authorities have been more and more urgent for this to be done, and justly so; for otherwise that gas frequently causes accidents (by choking) to the men employed at the works, and is at the same time an intolerable nuisance to the neighbourhood. Simply carrying the gas away by a chimney, or even across a fire, does not suffice, because in the latter case the hydrogen sulphide, which is at any rate greatly diluted by carbon dioxide, will not burn, owing to the presence of so much steam (p. 322). We shall see below how this can be avoided.

The number of apparatus proposed, or even actually employed, for working gas-liquor is extremely great; and a complete enumeration of them is not even to be attempted in this treatise. Most of them, even of those that have been in practical operation, are more or less unsuitable and obsolete. Hence not even the apparatus proposed by the author himself in a former treatise* will be mentioned here, and only such will be described as (excepting only the first) have been actually seen at work within the last few years by the author himself or thoroughly trustworthy informants of his.

Fig. 72 is a sketch of the apparatus of Elvers and Müller Pack for making liquor ammoniæ direct from gas-liquor. We have not reproduced the original sketch, which is somewhat difficult to understand, but placed the parts separately alongside one another, to make the principle clearer. For the same reason all supports, carrying-walls &c. are left out, and even the setting of the first boiler is only sketched in dotted outline. A and A' are cylindrical iron boilers, A' being placed sideways and above A, which alone is directly heated by the fire. A is surmounted by a dome, to which are attached an air-valve *v* for avoiding a collapse of the still by the atmospheric pressure on cooling, and the gas-delivery pipe *a*. The latter is carried first up, then downwards, and enters A' near the bottom, continuing into a pipe running all along the bottom and perforated with many holes, through which the vapours from A get into A'. The liquid in A' can be run into A by means of the wide pipe and valve *m*, which can be cleaned from deposit

* Destillation des Steinkohlentheers (1867), p. 138 *et seq.*

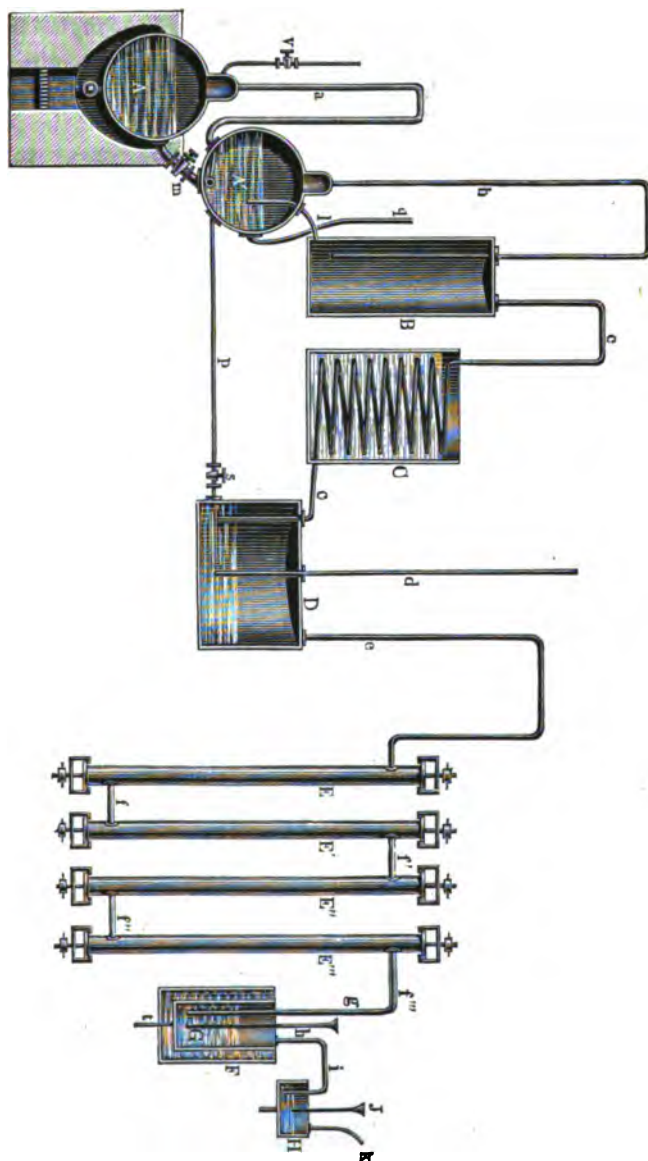


Fig. 72.

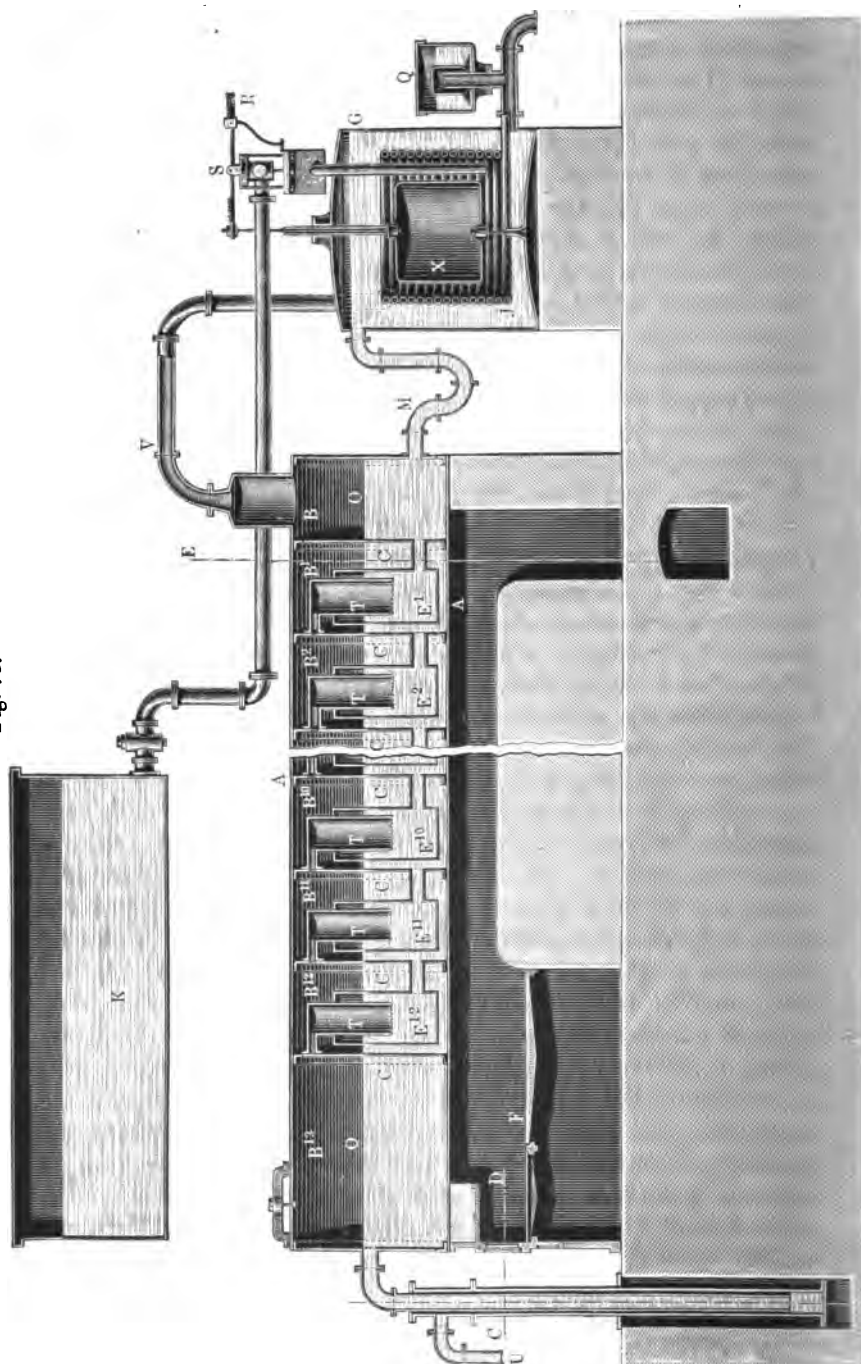
by means of a suitable contrivance. The vapours arising in A' first ascend in *b*, then descend into the vessel B down to within 12-inches from its bottom; the liquid condensed in B runs through *l* into A' below the level of the liquid there. From B the vapours enter the worm C, and through *c* the closed box D. From this the condensed liquid can be run back into A' by the tap *s* and the pipe *p*. D carries a safety-tube *d*, and a pipe *e* for taking away the uncondensed gases. These, now mostly freed from moisture, pass into the four cast-iron pipes E E' E'' E''', connected alternately at top and bottom by the pipes *f f' f''*; they are open at both ends, and closed by plates tightly screwed down. From E''' the gas travels through *f'''* and *g* into the leaden absorbing-vessel G, placed in a cold-water tank F; here also a safety-pipe *h* and a discharge-pipe *t* are provided. The residual gas gets through *i* into a small absorbing-vessel H, with safety-pipe J; and *k* carries the incondensable gases into the outer air.

First the still A' is charged by the pipe *q* with about 1000 litres of gas-liquor, contained in a higher store-tank; and this is at once mixed with a sufficient quantity of lime through a special aperture. The slide *m* is opened; the condensers C and F are charged with cold water, the pipes E E' E'' E''' with freshly ignited wood charcoal in pieces of the size of a walnut; and the covers are screwed down. G is charged with 60 or 65 litres of water, H with $\frac{1}{2}$ litre. When the liquor mixed with lime has flowed from A' through *m* into A, *m* is closed and the fire is lighted. The fire-gases travel along one side of the boiler, return along the other, and then go to the chimney. When the contents of A begin to boil, first the air is expelled and passes in bubbles through the water in G and H; A' and the pipes are filled with vapours and get heated. Gas-liquor is now run through *q* into A'; by the cooling thus produced the liquor in D is sucked back into A' through *c* and *b*, and air enters at *d*. When 1000 litres of gas-liquor have run into A', milk of lime is again added and well mixed, whereupon the fire is started again. The ammoniacal vapours from A escape through *a* into the liquid in A', traverse this from the many small holes of the pipes, and give off part of their ammonia to it. A portion of the steam is condensed in B, the water running back into A' through *l*, along with the volatilized salts. From B the vapours pass into C, where most of the water, together with a portion of the ammonia, is con-

densed. The condensing liquid serves for washing the ammoniacal vapours and especially for condensing the salts carried away with them. The uncondensed vapours pass through *e* into the charcoal purifiers, which absorb the impurities mixed with the ammonia gas. In *G* the pure ammonia gas is condensed by cold water, and liquor ammoniæ is obtained. The last remnant of the ammonia is condensed in *H* (?); the incondensable gases escape through *k*.—When the still *A* is worked off, the residue is discharged, and it is recharged from *A'*. The liquor now re-aspirated from *D* into *A* clears the worm *C* &c. from any deposit. If in *G* and *H* ordinary water, not distilled, has been employed for absorbing the ammonia, the precipitate of calcium, magnesium, and aluminium (?) salts formed must be allowed to settle, in order to obtain a clear, marketable product. Each operation takes 4 or 5 hours; and from 1000 litres of gas-liquor of 3° Baumé is obtained 100 to 110 kilogrammes of liquor ammoniæ of 22° Baumé (= sp. gr. 0.924).

Equally intended for the manufacture of liquor ammoniæ is the apparatus of Solvay, fig. 73 (p. 330). It consists of a still *A*, divided by partitions *C* into a number of compartments. Each compartment contains a tank *E*, connected with the next compartment at the bottom by a pipe. In the upper part of each compartment is fitted a pipe *T*, which is enlarged below and carries the vapours into the liquid of the next tank. The fireplace is at *D*. The ammoniacal liquor comes from the store-tank *K*, and goes first into a small vessel *G*, in order that the feed may be regulated by means of the valve attached to the lever *R* and the float *X*, and enters the still from the pipe *M*. Suppose this to be filled equally up to the level *O*. When vapours are evolved by heating the liquor, *e.g.* in *B*², they escape by *T* and force a certain quantity of the liquid into the annular space between *T* and *E*¹, over the margin of *E*¹ into *B*¹. Thus a certain quantity of gas-liquor has got from *B*¹ to *B*² by means of the vapours evolved in the compartment *B*²; in the same way the liquid travels from *B*² to *B*³ by means of the vapours evolved there; ultimately it arrives in *B*¹³, and leaves the last compartment by the pipe *U*. The progress of the liquid principally depends upon the proportion between the diameter of the dipping pipes *T* and the vessels *E*. The vapours arriving in the last chamber *B* are carried by the pipe *V* into a worm *J*, cooled by ammoniacal liquor, and afterwards through a washing-tank *Q* into the absorbing-apparatus. The float *X* regu-

Fig. 73.



lates the feed of liquor into the still; it sinks as liquid within the condenser is heated by the evolved vapours, and allows a larger quantity of liquor to enter through the valve S if the distillation goes on more quickly. When the firing is interrupted, no vapours are given off, the liquor ceases to pass from one compartment into another, and the level of the liquid rises; at the same time the float rises; and the valve S ultimately shuts off the feed of liquor entirely. Solvay's apparatus is especially intended to concentrate weak gas-liquor up to a strength of 15 per cent. NH_3 . According to Hanrez, the dimensions of apparatus hitherto constructed are sufficient for concentrating, every 24 hours, 12, 24, or 48 cubic metres (say tons) of gas-liquor of 2 or 3 degrees Baumé to the above strength, with a consumption of 27 to 36 kilog. of fuel per cubic metre. The hot water running away from U can be utilized for a preliminary heating of cold gas-liquor.

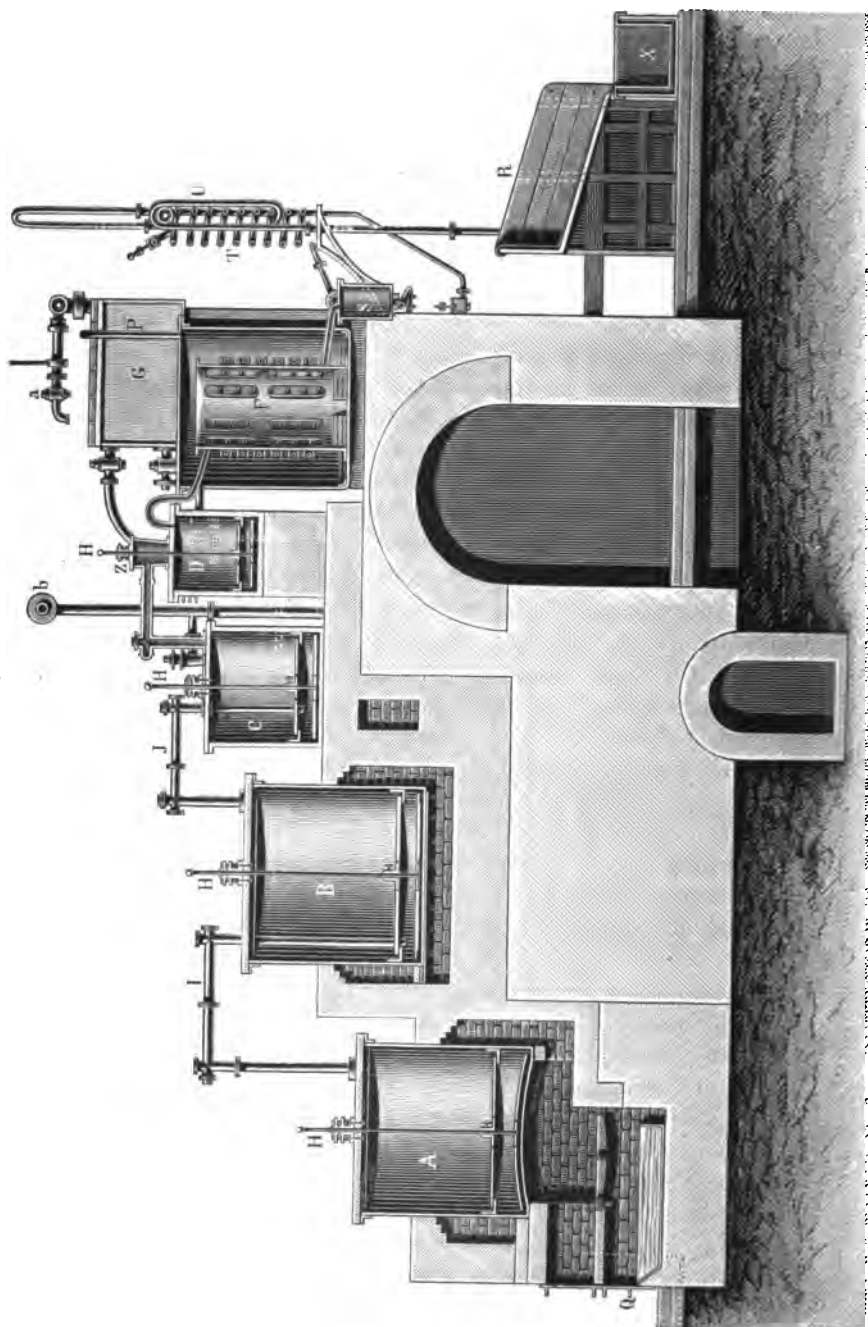
We must also mention that ammonia-apparatus which Solvay constructed for his system of manufacturing alkali by the ammoniacal process*; but it is not so well adapted for gas-liquor.

The apparatus of Mallet, which is employed by the Paris Gas Company, serves both for liquor ammoniac and for ammonium sulphate. It is represented in fig. 74 in longitudinal section, in fig. 75 half seen from above, half ground-plan, in fig. 76 back elevation. It consists of two similar sets, each of 3 stills A, B, and C, holding above 1000 gallons apiece, A and B being heated by direct fire. They are provided with agitating gear H H, passing through glands in the covers, for mixing the gas-liquor and lime and for preventing any burning on. C serves for washing the vapours from B, and is at the same time heated by these. From D the vapours enter a worm, about 70 or 80 feet long, placed in the tank F and cooled by gas-liquor. The liquid here condensed flows into S, and thence into the collector Y. The gases leave the upper part of S and pass through an air-cooled worm T, the pipes U (provided with a safety-apparatus), and into the absorbing-vessel V. The products condensed in T run back into Y.

The gas-liquor, freed from tar, is drawn through the tap *a* into the measuring-vessel G, which at the bottom is connected by a tap with the cooler F; a pipe branching off at the top, leads to the milk-of-lime pan E. The vessels A, B, C, D are connected at the bottom by the pipes K, L, N, and at the top by the pipes I, J,

* Compare Lunge, *Manufacture of Sulphuric Acid and Alkali*, vol. iii. p. 26.

Fig. 74.



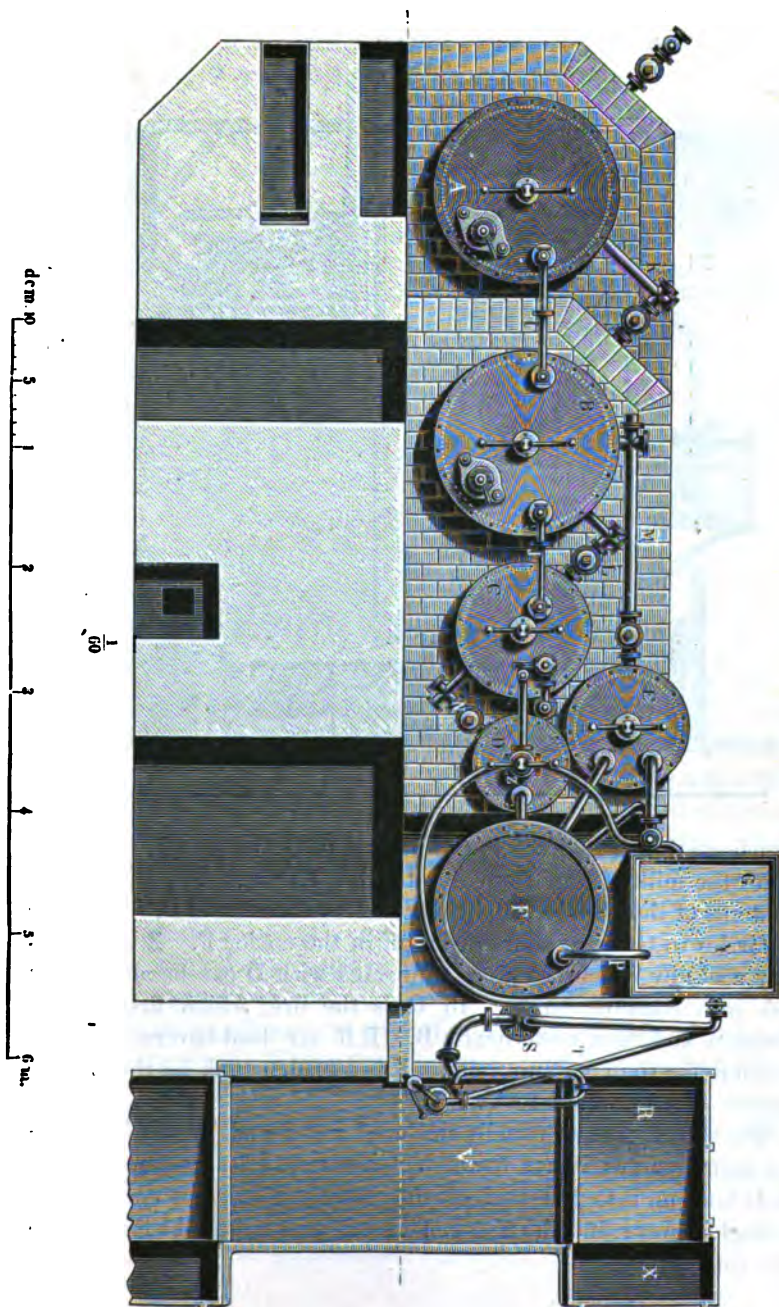
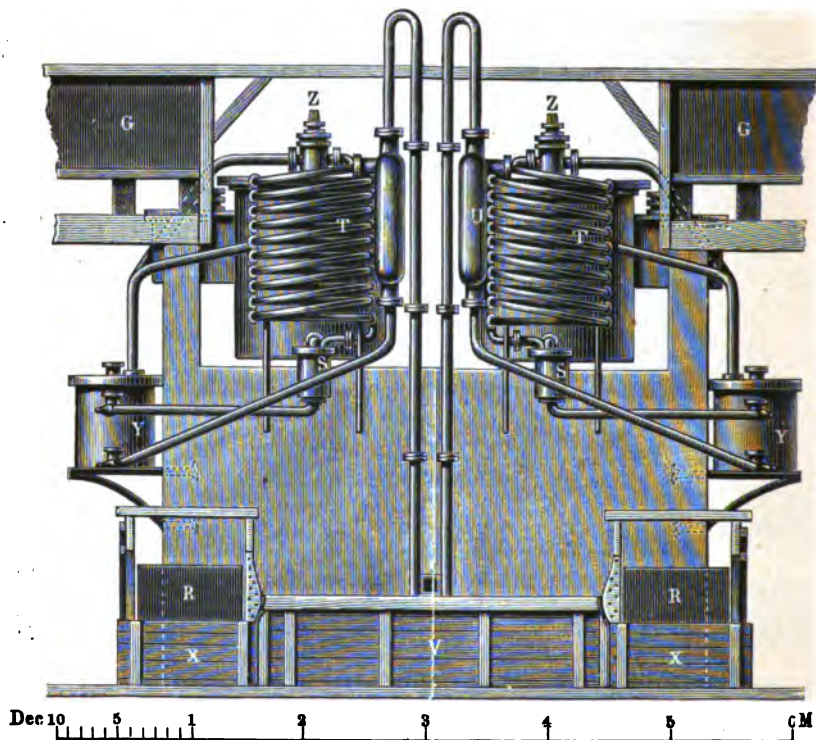


Fig. 75.

Fig. 76.



which reach nearly down to the bottom of B and C. The pipe M takes the milk of lime from E into B. Through the pipe O the contents of the vessel Y can be emptied into the vessel D. The pipe P carries to G the vapours given off in the cooler F. Z is a three-way cock, by which the pipes connected with D can be alternately put into communication. In Q is the fire, which first travels round A and then underneath B. R R are lead-covered wooden drainers for the ammonia salts. X is a leaden tank for the mother liquors which go back to V.

The saturators are usually made of wood and lined with lead; the ammonia gas issues through a horizontal lead pipe, lying at their bottom, into the acid or the water. The saturator has an air-tight cover; and the non-condensed gases escape through a pipe into the chimney.

If caustic ammonia is to be prepared, before distillation a quantity of lime sufficient for decomposing all the ammonium salts must of course be put into the still, to avoid contamination of the product [but this cannot be effected by the employment of lime alone!]. For making ammonium chloride or sulphate much less lime is required; and sometimes none at all is employed, the small quantity of fixed ammonium salts being given up as lost.

In actual practice* only a small portion of the gas-liquor in E is mixed with lime, half an hour before the operation; most of the liquor is run from G into F, where it serves as a refrigerant and is itself heated in the process; for this purpose it enters the vessel at the bottom and leaves it at the top. The stills are provided with safety-valves and water-gauges. At the end of the process the liquid is run away into a main drain.

The worm in F is 2 inches wide, and has nine coils. The worm T, when, instead of liquid ammonia, sulphate is made, is replaced by a cylinder 10 feet high and 4 feet 6 inches wide, into which the gas-delivery pipe from S enters and passes down nearly to the bottom. This cylinder is kept about one third filled by means of an overflow-pipe shaped like an inverted siphon; the overflowing liquid is collected in Y, like that coming from S. From that cylinder the gas passes first through an iron pipe, provided with a Welter's safety-tube to prevent any liquid from being forced back by atmospheric pressure, and then into a large lead tank, into which it issues from two lead pipes, lying at the bottom and perforated by many holes. This tank is two thirds filled with sulphuric acid of 116° Tw. †, and provided with a roof-shaped cover, from which the escaping gases (carbon dioxide and hydrogen sulphide) are carried into the chimney by means of a wood conduit. The sulphate crystallizing out is fished out from time to time, drained on sloping lead plates, and dried in a stove or upon metal plates heated by some waste heat.

As soon as a sufficient quantity of liquid has collected by condensation in the vessels Y (say once an hour), the three-way cock Z is for some minutes adjusted so that the gas from D passes no longer into the worm F, but into Y (this is best seen from figs. 74 and 75).

* The following details are unpublished observations of the process as actually carried out at La Villette, Paris.

† When such acid is employed, the temperature of the entering gas must be 80° if the sulphate is to crystallize out continuously.

Its pressure forces the liquid from Y through O into D; so that no pump is needed for this. The pipe O must reach down to the bottom of Y. Every three hours the contents of A are run off, and those of the succeeding stills B, C, and D run a stage lower down.

At La Villette a daily quantity of 10 tons ammonium sulphate is manufactured in 10 Mallet's apparatus, and 5 tons liquor ammoniæ in 4 apparatus. The gas-liquor averages $2^{\circ}9$ Baumé, and yields 7 kilog. sulphate per cubic metre; it is a mixture of the liquor from the hydraulic main (50 litres per ton of coal distilled) with that from the scrubbers &c.; 60 to 80 litres of lime is used per cubic metre of gas-liquor. Each ton of coals distilled is supposed to yield 2.2 kilog. NH_3 , = 8.5 kilog. ammonium sulphate. Each double apparatus requires one attendant and, for two fires, 10 hectolitres of coke per day.

One drawback of this apparatus is, that no provision is made for dealing with the hydrogen sulphide; it also contains a number of unnecessary complications.

The question of dealing with the sulphuretted hydrogen is grappled with in England as will be seen from the following description of some of the largest ammonia-works in the country:—

Fig. 77 gives a sketch of the apparatus employed at a London works where 100,000 gallons of gas-liquor are worked up per day, representing the product of 600,000 tons of coal per annum. The liquor arrives in canal-boats A, and is pumped up by the pump *a* into a large settling-tank B, where it remains for 24 hours. The liquor is pumped by the donkey-pump *b* into a Coffey still C, 30 feet high, 12 feet long, and 5 feet wide, into which steam of 2 atmospheres pressure is blown by 5 tubes. Here the volatile ammonium compounds are separated from the water and the non-volatile salts, which are usually run away into the canal because they only contain 3.5 per cent. of the NH_3 and do not pay for working off with lime (should this be intended, the residual liquid must be mixed with lime in a separate apparatus and again distilled in a Coffey's still). The volatile ammonium compounds pass out of the top of the still through a $2\frac{1}{2}$ -inch worm perforated with numerous $\frac{1}{2}$ -inch holes, into the cylindrical saturator D, made of strong lead (20 lb. per superficial foot), the lower two thirds being strengthened by strong planks bound with iron hoops. It is 6 feet high and 10 feet wide, and is filled up to two thirds of its

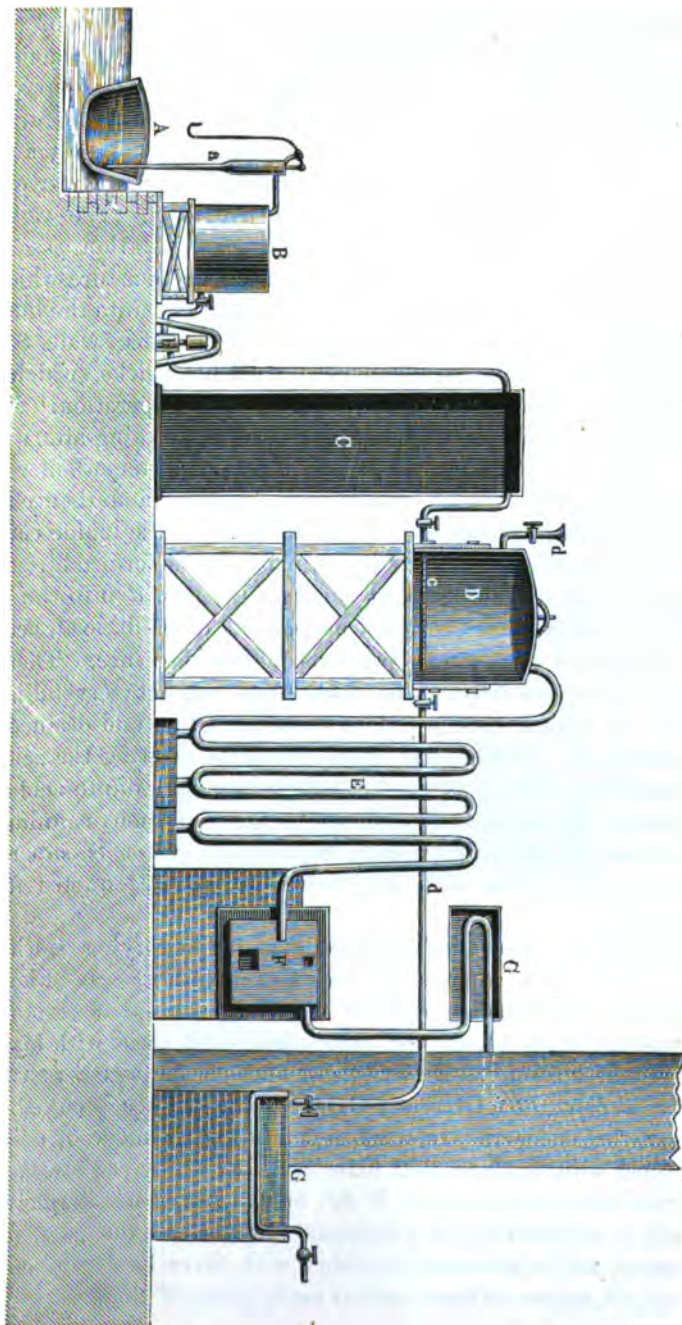


Fig. 77.

height, by means of the funnel-tap *d*, with a mixture of equal parts of brimstone acid of 140° Tw. and water, which remains in the apparatus till it is completely saturated. The acid is purposely diluted, to prevent the salt from crystallizing within the saturator. When the saturation is completed, the liquor showing only a very faint acid reaction, steam is blown through for a quarter of an hour, to drive off all the sulphuretted hydrogen. The vapours evolved in this process and during the whole operation pass first through the air-condenser E, to condense the moisture which is carried along, and then through a 7-inch metal pipe into the burner F. This is a square brickwork chamber, about 5 feet wide, 8 feet long and 4 feet high, loosely packed with fire-bricks, which are made red-hot before the commencement of the operation. Here the hydrogen sulphide takes fire, and is kept burning afterwards by its own heat. The hot gases pass through a steam-boiler (indicated at G), where their heat is partly utilized, and thence into a chimney, in which no smell at all of hydrogen sulphide can be perceived [but what becomes of the sulphur dioxide formed?]. The solution of salt is run from D through the pipe *d* into the lead pans G, 8 feet in diameter, 2 feet deep, made of 20-lb. lead, heated by a steam-coil working at two atmospheres' pressure. There is no smell perceived here. The ammonium sulphate crystallizing is fished out with a wooden spade, washed a little, and drained on a wooden floor. The mother liquor serves for diluting the acid in the saturator. This process, *i. e.* saturating with dilute acid and evaporating the solution, is preferred to the continuous running-in of acid and fishing-out of salts, because the result is superior. This perfectly agrees with the statement (p. 324) quoted from Watson Smith.

Coffey's still was originally constructed for rectifying spirit of wine, but has been employed for many similar purposes. Fig. 78 represents the shape employed for spirit of wine: that employed for ammonia is essentially the same; but wood lined with lead is substituted for copper. It consists of an oblong vessel B and two superposed columns CDEF and GHIK. The former is called the analyzer, the latter the rectifier. The whole is made of 6-inch wood lined with lead, so that little heat is lost by radiation. B is divided into two chambers, B' B'', by the horizontal diaphragm *d*, which is perforated with numerous apertures for the passage of the vapour, and is moreover furnished with several valves opening upwards, *e e*, in case of more vapour being given off than can escape

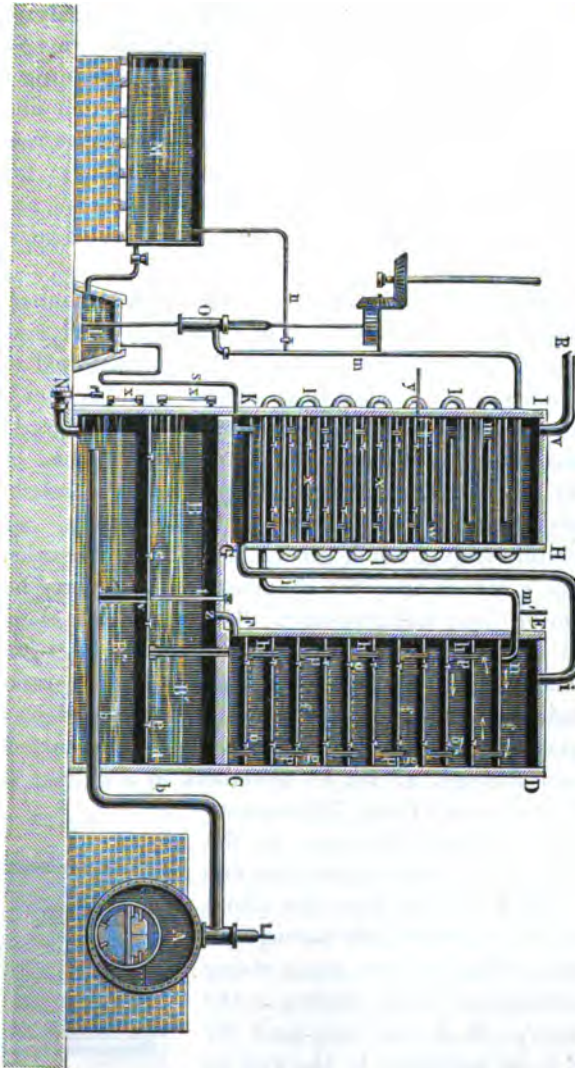
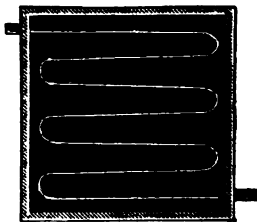


Fig. 78.

through the apertures. A pipe *v* reaches nearly to the bottom of *B''*, where it dips into an hydraulic lute; it can be opened or shut off by a valve attached to the rod *t*, which passes through a stuffing-box at the top. *xx* are liquor-gauges for *B'* and *B''*. The analyzer *CDEF* is divided into 12 chambers *fff* by sheet-iron diaphragms *gh*; these also contain many perforations, as well as valves opening upwards *oo*; also overflow-pipes, *p*, projecting about an inch above each plate, so that a corresponding depth of liquid always remains on each diaphragm. The pipes *p* reach down to the next lower diaphragm, where they dip into hydraulic lutes (traps), so that no steam can escape through them; they are inserted at alternate ends of the diaphragms.

The rectifying-column, *GHIK*, is in a similar manner divided into 15 chambers. The lower ten of these are filled exactly like those of the analyzer, their diaphragms being furnished with perforations, valves, and overflow-pipes. The top chamber of these ten is covered by a metallic diaphragm with only one large opening at *w* for the passage of vapour, and an overflow-pipe *s*. *w* is surrounded by an upright flange which prevents the return of the most rectified liquid into the lower part of the column. *s* is closed by an hydraulic trap of much greater depth than the others, from which a pipe *y* carries away the condensed but still very hot liquid into a worm or other refrigerator*. The upper five chambers, *v*, are formed by plain unperforated diaphragms, with openings at alternate ends, large enough for the passage of both vapours and liquid; their only use is to cause the vapour to pass along the pipe *m* in a zigzag direction, so as to enlarge the cooling-surface. The pipe *m* runs through all the 15 chambers in a zigzag, as shown in fig. 79, the bends *ll* (fig. 78) forming the connexion between the pipes of the different chambers, thus constituting one continuous pipe, leading from the pump *O* upwards, then downwards through all the chambers of the rectifier, again rising upwards outside and finally ending in the analyzer at *n'*. *M* is the store-tank for the liquid to be rectified; *L*, the well for the pump *O*, which is working continuously and supplies rather

Fig. 79.



* This can be omitted in rectifying gas-liquor, except when liquor ammoniac is to be made in the apparatus itself.

more liquor than is necessary to keep the apparatus going; the surplus runs back into M through a pipe, *n*, furnished with a stop-cock by which the operation can be exactly regulated. The necessary heat is supplied by the steam from the boiler A; the steam-pipe *b b* within the receiver B'' branches into a number of smaller perforated pipes (these are not shown in the diagram).

An operation is commenced by setting the pump O in motion, till all the zigzag pipes, *m m*, are filled and the liquor passes into the analyzer at *n'*. The pump is then stopped, and steam is let into the still through *b b*; it passes up through the receivers B' B', then through the pipe *z* into the analyzer, passes into *i*, in which it descends and enters the bottom of the rectifier at G. It then rises through the chambers X X, envelops the zigzag pipes, and heats the liquor in them. When the attendant by feeling the bends *l l* perceives that perhaps eight or ten of the chambers of the rectifier have become heated, he again sets the pump to work. The gas-liquor, now nearly boiling-hot and always in rapid motion, flows from *n'* into the analyzer and downwards in this through the overflow-pipes *p p* from chamber to chamber, as shown by arrows in the top chambers. It cannot pass down through the perforations of the diaphragms, whose number and size is so regulated that they are no more than sufficient to afford a passage for the vapours upwards when under some pressure. Steam and vapour thus pass in each chamber in numerous jets through a thin stratum of liquor, and so completely expel all volatile ammonium salts that in B no trace of these can be found any more. When the water-gauge *x* shows that B' is nearly full, the valve at *t* is opened and the contents of B' are discharged into B''. When this is also full its contents are discharged by the cock N', the contents of B' are again run into B''; and in this way the process goes on as long as there is any liquor to be distilled. The boiling-hot spent liquor running from B' serves to raise the temperature of the water intended for feeding the steam-boiler A.

Having now followed the liquor in its course onwards to the point where it is deprived of all volatile ammonia, we shall trace the course of the steam. This in its passage through the 12 chambers of the analyzer takes up a large quantity of ammonia, and is partly condensed to water. The remaining mixture of steam and vapour at *i* passes into the rectifier, envelops the pipes *m m*, heats their contents, and by condensation parts with more of its watery

portion, which condenses in a boiling state on the various diaphragms. What escapes through *w* is nearly pure ammonia; and this, after being further cooled in *vv* and having lost the last portions of water, escapes through *R* into the saturator *D*, fig. 77.

If liquor ammoniæ is to be made, the gas-liquor must be mixed with lime. In this case less steam is blown in, so that the chambers *vv* remain at the ordinary temperature and from the pipe *y* strong liquor can be obtained at will, passing it first, by preference, through a refrigerator. The water condensing lower down in the rectifier contains a little ammonia, and hence runs back through *s* into *L*, in order to be pumped up again by *O*.

The operation is mainly regulated by observing the thermometer *m'*, which shows the temperature of the liquor issuing from *n'*. Whenever the liquor is too hot, more liquor is let into the apparatus, or *vice versa*, which can be effected at will by the overflow-cock *n*.

According to the requirements of a work, Coffey stills are made more or less wide and high, with a corresponding number of steam-pipes and chambers. Such stills hardly pay when less than 10,000 gallons of liquor is worked up per day.

At another ammonia-works than that just described the Coffey stills are from 18 to 25 feet high, 6 to 10 feet long, and 1 or 2 feet wide, with 20 or 30 diaphragms, 3 inches apart; at the top there is a space of 6 inches, at the bottom another of 2 feet (in lieu of the receiver *B*, fig. 78). Steam of $1\frac{1}{2}$ to 2 atmospheres is employed. The liquor at that works is $7\frac{1}{2}^{\circ}$ Tw. strong; the solution of ammonium sulphate is boiled down to 52° Tw. before it is allowed to crystallize.

At another ammonia-works the gas-liquor is distilled in horizontal cylindrical stills, *A* (fig. 80), holding 10,000 gallons and charged with 7000 gallons each time. The heat is applied by somewhat superheated steam in a closed coil. It is preferred to employ gas-liquor of not less than 5° Tw., or, say, 10 ounces, without addition of lime. Experience has shown that the loss, including the fixed ammonia, is always = 1 ounce per gallon, so that from a 16-ounce liquor sulphate equal to 15 ounces is obtained (?). The vapours issue through a lead coil *a*, perforated with $\frac{1}{4}$ -inch holes 6 inches apart, into a lead saturator *B*, strengthened by planks and hoops (compare p. 336). This is charged with sulphuric acid of 47° Tw. from the tank *C*, which is filled by means

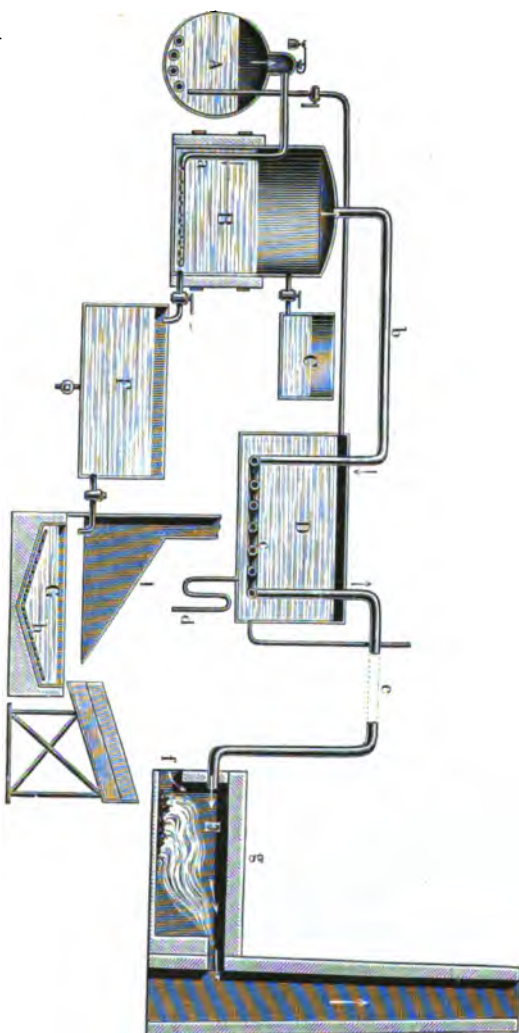


Fig. 80.

of an air-pressure apparatus (acid-egg)*. The vapours escaping from B pass through the 8-inch pipe *b* into the closed vessel D, where they circulate in the coil *c*; the liquid condensate runs away at *d*. D is filled with gas-liquor, which is thus heated and

* Compare Lunge's 'Manufacture of Sulphuric Acid and Alkali,' vol. i. p. 393 *et seqq.*

serves for feeding A. From D the vapours issue at *e*; they are now cooled by air through travelling round the works in a pipe 300 feet long, in which nearly all the water condenses, and are at last conveyed into the furnace E, where a fire is kept up with small coal. Air enters at *f*; and the combustion of the hydrogen sulphide is completed by causing the gases to pass along the red-hot arch *g*. The sulphur dioxide escapes into the air.

The solution of ammonium sulphate from B runs into the settler F ($9 \times 9 \times 2$ feet), and from this, through a tap 4 inches from the bottom, into the boiling-down pan G (20 feet long, 5 feet wide, 2 feet deep, half of this being straight, half conical). The heat is applied by means of the steam-coil *h*; the vapours pass away by the hood I*.

Fig. 81 is a sketch of the apparatus in operation at a large London works where lime is employed and where continuous saturation is preferred. The gas-liquor is pumped at *a* into a column B, which it traverses from the bottom to the top in many pipes, the empty space being filled by the hot gases from the saturator A, which thus raise the temperature of the liquor. The latter now arrives in a square iron column C, about $3 \times 3 \times 20$ feet, packed with retort-graphite. In this the gas-liquor descends, whilst steam enters through *a'* and expels the volatile ammonium salts, which escape at *b*. The liquor passes into D, a small reservoir intended to feed the horizontal still E, in which it is mixed with lime; the steam let into this effects both the agitation and the distillation. The vapours escape at *b'* and unite with those from *b* before passing into the saturator A. This is a large lead vessel, continually fed with a thin jet of sulphuric acid of 140° Tw. It is adjoined by the box *d* open at the top; the partition does not reach quite to the bottom, but is always kept luted by liquid. The sulphate of ammonia at once separates in a solid form, is raked out on the sloping bottom of A into *d*, fished out with perforated spades, and drained on the drainer *c*. The mother liquor always runs back into A; the drained salt at once goes into the market. The hot mixture of steam and gases, escaping from A, first passes through *f* into B in order to heat the gas-liquor (as mentioned above), then through *g* into a vessel F, where it is forced through

* An exact description and diagrams of the steam concentrating-pan, merely sketched here, is given in Lunge's 'Manufacture of Sulphuric Acid and Alkali,' vol. i. p. 503 *et seqq.*

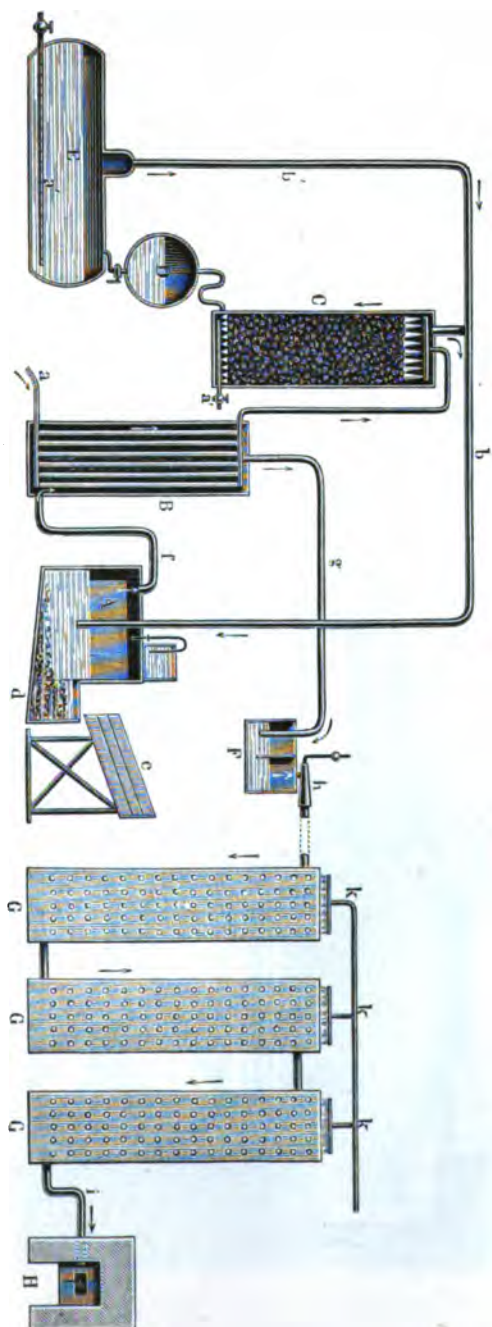
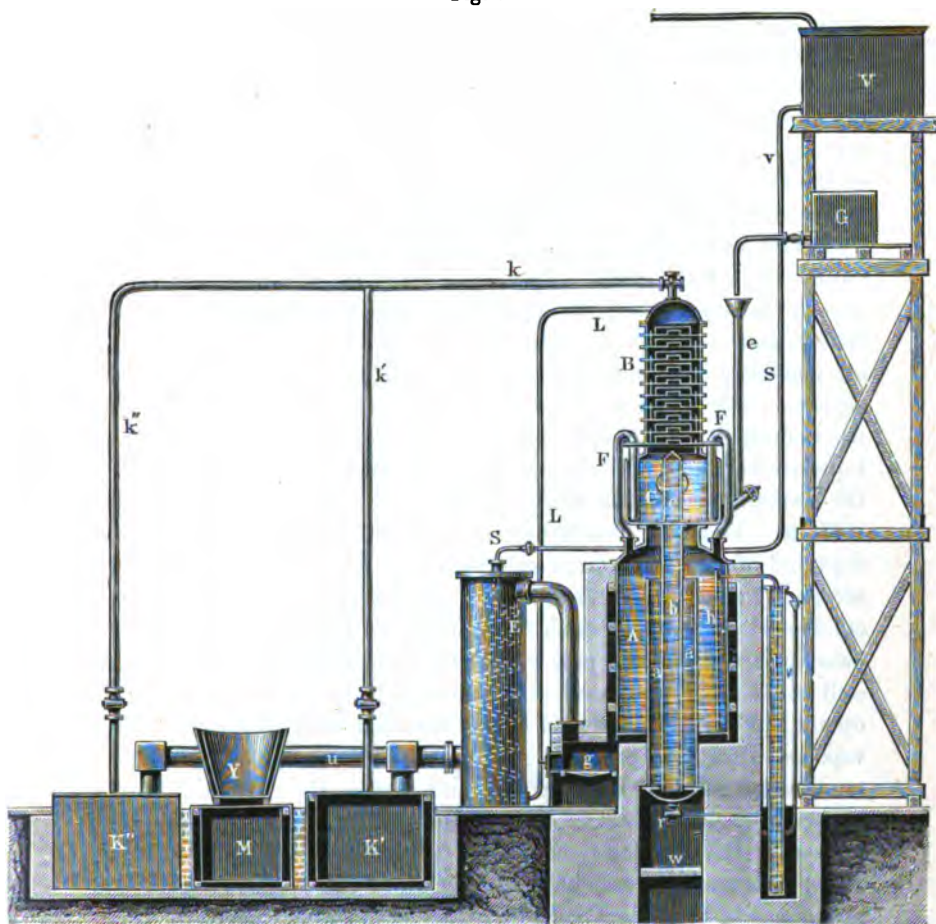


Fig. 81.

Fig. 83.



One of the best apparatus for distilling gas-liquor is that of H. Grüneberg. His older apparatus* has been superseded by a different form †, which alone we shall describe here, as it is most successfully working at 13 factories (September 1880). One of its principal advantages is, preventing the lime from forming hard crusts on the heating-surface of the stills, and removing the lime residue without any loss of time. Figs. 82 and 83 are partly ele-

* German patent No. 35, July 13, 1877; *Chemische Industrie*, 1878, p. 50.

† German patent, No. 9392; also patented in the United Kingdom.

vations, partly sections. An upright cylindrical still A, heated from the fireplace *g* by flues surrounding it, has within it a vertical cylindrical tube *a a*, the bottom of which, extending below the bottom of the boiler, beyond the heating-zone thereof, is closed and furnished with a blow-off cock, *r*, and a perforated screen, *d*. The upper end of this tube, reaching nearly to the top of the boiler, is open to the vapour-space in the boiler. Above the boiler is the vessel C, charged with milk of lime from the tank G by *e*, and above this a rectifying-column, B, of the description often employed in spirit-stills. The pipes FF extend from the top of A into the lime-vessel, ending near its bottom with numerous small perforations. By these pipes the vapours generated in the still are conveyed into the milk of lime, and keep this continuously agitated; they then pass through the successive compartments of the column B. This column is supplied by the pipe L with gas-liquor, which descends from one compartment to another, while the vapours ascending from A through C are intimately mixed with it. Thus the descending gas-liquor is gradually heated and deprived of its volatile ingredients, whilst the ascending vapours are partly condensed and mix with the descending liquid; the uncondensed gases, along with those liberated from the liquid in B, pass away through the pipe *k*. From the bottom of B the liquid, still containing the non-volatile ammonium salts, flows through an opening into the lime-vessel C and is mixed with its contents, the vapours from FF producing a continuous agitation. Here the ammonium salts are decomposed, and part of the ammonia passes along through B into *k*. The liquid, still containing ammonia, passes, by the overflow-pipe *c b*, to the bottom of the boiler-tube, *a*, which is removed from the direct action of the fire, so that there is no danger of the lime becoming attached to the surface of the tube, neither can the material of the tube, or that of the lime-vessel, be injured by overheating.

From the bottom of the tube *a* the liquid rises through the perforated plate *d*, flows over into the outer boiler A and is heated in the same; the gases and vapours evolved are conveyed by FF into C, as above mentioned. From the bottom of A the liquid, now entirely deprived of ammonia, overflows through *h* into a deep vessel J, the contents of which operate as an hydraulic seal, and from this through N to a drain. All this proceeds *continuously*—the feeding with gas-liquor by L, the overflowing of the

spent liquor through N, and the escape of the ammoniacal vapours at *k*.

The apparatus, fig. 82, serves for producing a concentrated solution of ammonium carbonate and sulphide, *e.g.* for the ammoniacal soda process. The vapours rise through the cooling-pipe O into a worm in the vessel D, where they are condensed to the condition of (impure) liquor ammoniæ. This flows into a vessel E, whilst the uncondensed vapours and gases pass into a vessel H, whose contents form an hydraulic seal. The gas not condensed here escapes through P. The vessel D is closed; and the worm within is cooled by raw gas-liquor supplied from the reservoir V by the funnel-pipe X; after getting heated here, it passes through L into the column B. The cooling-pipe O acts as a regulator of the concentration. The more cold water is supplied to its casing by the pipe R, the greater is the condensation of aqueous vapour in O, the condensed water flowing back into B, and the more concentrated is the residual fluid which passes to the worm in D. Thus the degree of concentration of the liquid ammonia can be regulated at will.

If it were intended to make real liquor ammoniæ, the vapours issuing from the column would have to be passed through a number of vessels filled with milk of lime and finally into a cooled absorbing-vessel.

The apparatus fig. 83 serves for producing ammonium sulphate. The gaseous mixture passes through *k* and alternately *k'* and *k''* to the saturators K' and K'', containing sulphuric acid. Considerable heat is evolved by the combination of this acid with ammonia, so as to vaporize the excess of water present in the acid [provided the latter be not much under 130° Tw. strong]. The vapour thus generated, together with offensive gases (CO₂, H₂S, &c.), pass along the large pipe *u* and into the vessel E, where their heat is utilized for a preliminary heating of the gas-liquor which passes at S into a coil or set of pipes, in order to be conveyed through L into the column. From E the uncondensed gases pass through *v* into a fireplace *g*, where the offensive gases are consumed. The ammonium sulphate separated in K' and K'' is put into the drainer Y, provided with a perforated false bottom; the mother liquors collect in M.

The coal used averages one cwt. for each ton of gas-liquor passed through the apparatus, the lime 15 to 20 per cent. of the ammo-

nium sulphate produced. Two men can attend to an apparatus capable of distilling ten tons per diem. Such an apparatus, without the lime-vessel, is 10 feet high and 5 feet wide; the column and lime-vessel add another 8 feet. It costs from £175 to £200.

The following estimate is given by Dr. Grüneberg for producing sulphate of ammonium with his apparatus, say, at Manchester, assuming a maximum cost of 24s. per ton for "11-oz." liquor.

	£	s.	d.
3500 tons of 11-oz. liquor, @ 24s.	4200	0	0
300 „ sulphuric acid, @ 85s. (less 5 per cent.)	1211	5	0
71 „ lime, @ 12s. 6d.	44	7	6
175 „ coals, @ 10s.	87	10	0
Labour, 2 men 50 weeks each, @ 25s.	125	0	0
Casks and packing for 389 tons, @ 8s.	155	12	0
Sundries, repairs „ „ @ 6s.	116	14	0
Depreciation on plant, £300; buildings, £150, total £450, at 10 per cent.	45	0	0
Interest on plant, buildings and land, total £550, @ 5 per cent.	27	10	0
Produce, 389 tons ammonium sulphate, costing or £15 9s. per ton.	6012	18	6

The present value at Hull is about £20, less 2½ per cent. discount and 1 per cent. brokerage.

Production of pure Liquor Ammoniae from crude concentrated caustic ammoniacal liquor.

We have more than once in the preceding pages spoken of this, and will here add a communication, received from Mr. Watson Smith, describing an apparatus especially intended for this purpose and in operation at Manchester. The sketch, fig. 83a, will illustrate it. The raw caustic liquid is put into a still *a*, 8 feet long and 4 feet in diameter, heated by a fire which is kept away from the bottom of the still by an arch and only circulates round the sides. For each charge of 600 gallons, containing 3½ to 4 per cent. ammonia, 2 cwt. of quicklime, previously slaked to a thick paste, is added, and a strong fire is made. The gases escape through a 2-inch pipe into the lead worm *b* (cooled outside by water), in which the aqueous vapour is condensed and flows back. In the descending branch *c* a little more water is condensed and collects

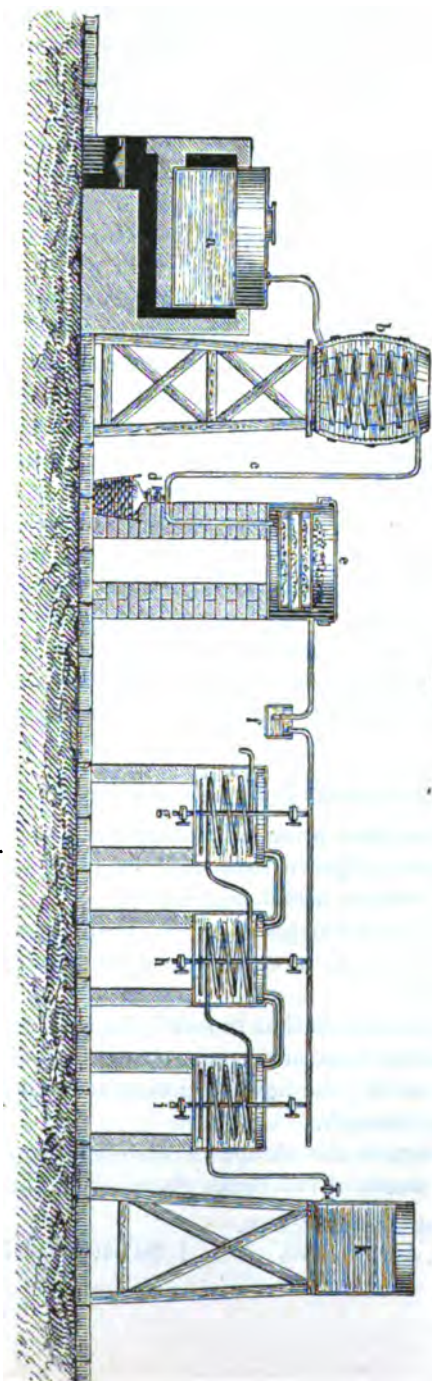


Fig. 88 a.

in the carboys *d*. The nearly dry gas is treated in the purifier *e* (6 feet long, and $4\frac{1}{2}$ feet wide) with slaked lime, to remove hydrogen sulphide, tar, &c. The top of the purifier is luted with lime putty, and is screwed down tightly; its contents must be renewed two or three times a month. From this the gas passes in a 1-inch pipe through a small washing-arrangement *f*, and then by means of india-rubber joints provided with screw clamps, at will into one of the three absorbers *g*, *h*, *i*, made of iron lined with lead, $3\frac{1}{2}$ feet square and 3 feet high, and provided with gauge-glasses. These vessels are charged with pure water; the gas issues into them from perforated rings of lead tubing lying at the bottom. The vessels are connected by gas-pipes; they also have an air-vent each; but of course this is only opened in the last one of the series. The contents of *g*, *h*, *i*, are cooled by water, which, coming from the tank *k*, is passed through all the absorbers by means of worms. After the liquor has become sufficiently strong, it is drawn off by taps into carboys, ready for sale. It should be clear, free from any greasy matter, and of sp. gr. 0.905, or at most 0.914. No traces of sulphides, indicated by lead acetate or sodium nitrocyanide should be present. (This description may serve to show how an apparatus can be constructed in a cheap and simple manner; but comparison with the preceding descriptions will show that it lacks some of the perfections of those more modern appliances.)

Recent Improvements in the Manufacture of Ammonia.

We shall in this place principally mention those proposals which have not had time to prove successful or otherwise, but which may at any rate contain useful suggestions.

Brullé and Leclerc * run gas-liquor in thin layers over a heated surface, and expose it to a warm current of air travelling in the opposite direction.

Rousseau † recommends that in rectifying ammonia by dephlegmation, the water be kept at a temperature of from 60° to 70° C. Below this, *e.g.* at 55°, the liquor begins to take up ammonia from the gases passing through.

Hegener ‡ prevents the escape of ammonia in charging with milk of lime by means of two tanks placed above the still. In the

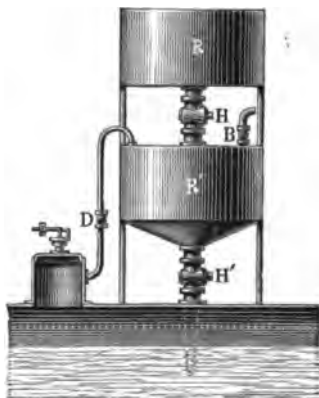
* Patent, No. 1086, March 13, 1880.

† French patent, Aug. 18, 1880.

‡ German patent, No. 11,669.

upper one (R. fig. 84) the lime is slaked and the milk of lime is let down into the lower one, R', by the cock H. During this the ammoniacal gases in R are conveyed to a special receiver by a pipe proceeding from the air-cock B. When the milk of lime is to be run into the still, the cocks H and B are closed, but H' and the steam-cock D are opened.

Fig. 84.



Young * conveys the ammoniacal vapours, evolved without using lime, along with air through a fireplace, thus burning the ammonium sulphide to sulphite and partly to sulphate. The gas passes into a suitable condenser. The ammonium sulphite dissolved is converted into sulphate by passing a current of heated air through the solution [as previously proposed by Laming]. If (as is always the case) the liquor does not contain enough sulphides to convert all the ammonia into sulphite, sulphur dioxide is mixed with the products of distillation before or after they have passed through the fire, or else the condensed liquid is neutralized with sulphurous or sulphuric acid. —If this process should turn out workable, a great drawback in the ordinary mode of burning the hydrogen sulphide will be done away with, viz. that sulphur dioxide is formed and escapes into the air. The principal difficulties to be overcome would appear to be:—1, the complete combustion of H_2S when mixed with so many other gases; 2, the possible combustion of NH_3 into N and H_2O ; 3, the condensation of the highly heated ammonia compounds diluted with air.

Gerlach † combines the working-up of gas-liquor with the ammoniacal soda process. This process, which belongs to the domain of alkali-making, has not found any practical application.

De la Martellière ‡ converts gas-liquor by means of aluminium sulphate into a solution of ammonium sulphate, which is drawn off clear from the silicic acid and alumina precipitate, and boiled down. This process does not appear very practical.

* English patent, No. 1310, March 30, 1880.

† Dinger's Journal, p. 223, 1882.

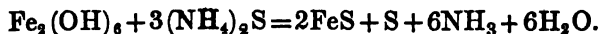
‡ English patent, No. 2963, July 19, 1880.

Removal of Hydrogen Sulphide.

The following is a synopsis of the various possible or proposed processes for this purpose, some of which have been already mentioned in the preceding descriptions.

1st. *Retaining it by lime during the distillation.* This consumes much lime, involves more complicated apparatus, and produces a fresh nuisance in the residual calcium sulphide. Moreover the action of the lime is always incomplete, even when used in excess.

2nd. *Retaining it during the distillation by ferric hydrate, as used in purifying gas.* The reaction is



Thus ferrous sulphide, sulphur, and free ammonia are produced; the two former remain behind and can be revived in the usual manner till the mass is rich enough in sulphur to be utilized in vitriol-works, or for the sulphur to be recovered by distillation. For the latter purpose Gerlach* employs superheated steam, as offering great advantages.

3rd. *Precipitating the ammonium sulphide before the distillation, by salts of iron or manganese †.* This is too expensive.

4th. *Absorbing the H_2S from the vapours by means of lime or iron oxide in the ordinary gas-purifiers.* This is possible, but expensive, and it is less complete than No. 1 or 2.

5th. *Burning it into SO_2 , which escapes into the air.* This is the usual process (compare pp. 338, 344, 346); but it is successful only when proper precautions are used, such as condensing the water and passing the gas along with air through a fire; the sulphur dioxide is, no doubt, a nuisance, but a much smaller one than the hydrogen sulphide.

6th. *Burning it to SO_2 , which is employed for producing sulphuric acid.* This process has been carried out for a long time by Hunt at Frizinghall near Bradford, and by P. Spence at Manchester. The vapours of SO_2 , produced as in No. 5, mixed with carbon dioxide, nitrogen, and atmospheric air, are worked for sulphuric acid in ordinary vitriol-chambers with the assistance of steam and nitrous acid. This process is said to have been practically successful ‡;

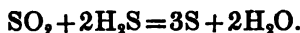
* German patent, 229, July 3, 1877. † Wagner's Jahresber. 1870, p. 749.

‡ Fourteenth and Fifteenth Reports on the Alkali Acts, by the Inspector, p. 46.

but it is very doubtful whether it covers the expense. There is much coke used; and the condensation of the acid is greatly impeded by the admixture of the foreign gases.

7th. *Burning the ammonium sulphide into sulphite &c.* This is Young's process, described on p. 353; the author is unaware whether it has yet undergone the test of practice.

8th. *Burning a portion of the H_2S and decomposing the SO_2 formed with the remaining H_2S into water and sulphur, thus:—*



This process has only become practical since Schaffner and Helbig brought the gases together in the presence of calcium chloride. It seems very likely to solve the question. The above process is described in detail, and explained by diagrams, in Lunge's 'Manufacture of Sulphuric Acid and Alkali,' vol. ii. p. 689 *et seqq.*

Château * describes the apparatus employed at Arcueil for deodorizing the gases evolved in the manufacture of sulphate of ammonia. They are aspirated by a fan-blast through a coke-column, 17 feet high, in which is spread a mixture of ferric oxide and calcium sulphate, constantly moistened by a solution of ferrous sulphate. Here ammonia and carbonic acid are retained. The gases on issuing out of the fan-blast pass over a thin layer of camphor [*sic*] and then into a combustion-furnace constructed by M. Perret. The grate-bars of the latter are only $\frac{1}{4}$ inch apart, and are so deep that they can be made to dip their lowest portion into a water-basin in order to cool them and retain their shape. The gas enters in the narrow space between the water-basin and the grate. The latter is charged with anthracite dust, which is partly carried away by the gaseous current, but is completely burnt in zigzag flues, made of fireclay flags, which soon attain a white heat. At this high temperature hydrogen sulphide, ammonium sulphide, cyanogen compounds, and any other deleterious gases are completely burnt, air being admitted by special openings for that purpose. The strong heat generated is employed for heating a steam-boiler. The apparatus is in regular operation, and is said to give very satisfactory results; but it does not deal with the question of removing the sulphurous acid.

* Bull. Soc. Chim. xxxvi. p. 195.

COMMERCIAL AMMONIACAL PREPARATIONS.

Liquor Ammonia (Caustic Ammonia, Spirit of Hartshorn).

The percentage of ammonia in this is nearly always ascertained by means of the hydrometer, for which the tables on p. 311 *et seqq.* may serve; but it must not be overlooked that these are valid only for the temperatures stated. In lieu of the figures for specific gravity, it is usual in Germany to employ the hydrometer of Baumé or Beck, in France that of Cartier; a table given in the appendix will permit the reduction of these degrees to specific gravities.

Technically pure liquor ammonia ought to be colourless, clear, and not smelling too much of empyreuma. Sulphides ought to be entirely absent, as shown by lead-paper. Pure liquor ammonia for pharmaceutical purposes ought to be free from chlorides and cyanides (in which case, when it is neutralized by nitric acid, silver nitrate produces no opalescence), and should be almost free from empyreuma. The latter is especially perceptible on neutralizing the liquid.

Kupfferschläger* proposes proving the presence of tarry matters in liquor ammonia by the red colour which is produced by pouring a few drops of it into a test-tube containing a few cubic centimetres of colourless nitric acid diluted with a quarter of its volume of water. According to Wittstein†, the pink colour does not arise if the nitric acid be at once supersaturated with ammonia, but only on partial saturation, and it is destroyed by an excess of alkali. Both chemists ascribe it to the action of nitric acid on aniline &c. Lehmann‡ many years ago made a similar observation.

The empyreuma can be removed by freshly ignited charcoal, or by distilling over potassium permanganate &c.

Liquor ammonia is employed for numerous purposes—in pharmacy, dyeing, calico-printing, for the preparation of colouring-matters and of many chemicals, and especially for Carré's and Linde's ice-making machines.

* Bull. Soc. Chim. xxiii. p. 256.

† Dingler's Journal, cxxiii. p. 512.

‡ Wagner's Jahresh. 1864, p. 195.

Sulphate of Ammonia.

Properties of the pure salt, p. 318. The commercial salt, when made with sulphuric acid free from arsenic and iron and by distilling the ammonia into the acid, will be white or at least light grey. The salt made by direct saturation of gas-liquor with sulphuric acid is usually grey or brown. We have seen above (p. 324) how such dark colour can be avoided by a special procedure in saturation. Even then a yellow colour may occur, from iron salts gradually accumulating, unless the saturator is cleaned out from time to time. Otherwise a yellow colour is caused by the presence of sulphide of arsenic, which can be avoided only by employing sulphuric acid as free as possible from arsenic.

The salt is now always sold according to its percentage of ammonia, which for chemically pure salt would be 25.75 per cent., and even in commercial salt is sometimes 24 or 25 per cent. The percentage is ascertained by the processes to be mentioned at the end.

In the English trade the strength usually stipulated for between buyer and seller is 23 per cent. NH_3 . As the manufacturers found that they could easily get up to $25\frac{1}{2}$ per cent., they brought this down to 23 per cent. by adding common salt or sodium sulphate; but some buyers object to this, in the sale-notes. (Private communication from Watson Smith.)

A very disagreeable impurity in ammonium sulphate is *ammonium sulphocyanide*. This is hardly found in such salt as is obtained by distilling gas-liquor with lime and absorbing the gas in sulphuric acid; but it may occur in the salt obtained by direct saturation of gas-liquor with acid, and it is more regularly found in the salt which is made by washing spent oxides from purifiers and evaporating the washings. The latter product contains frequently 25, sometimes up to 91 per cent. ammonium sulphocyanide*. Since that salt is very injurious to vegetation, and lessens the value of the ammonium sulphate, or even makes it quite unsuitable for manuring-purposes, such solutions ought never to be evaporated directly, but should be distilled with lime; calcium sulphocyanide might be extracted from the residue and worked up for sulphocyanides, which have now become articles of commerce. The detection of sulphocyanide in commercial sulphate is very easy, by the well-known red colour it gives with iron per-salts; even its quan-

* Esilman and Bell, Chem. News, xxxii. pp. 197 & 124.

tative estimation by a colorimetric process might be founded upon this reaction.

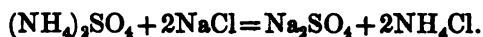
Most of the ammonium sulphate is employed as a manure; especially for the cultivation of beet-root it cannot be replaced by the cheaper nitrogen of nitrate of soda. Besides, it serves for preparing the other ammonium salts, and frequently for the preparation of liquor ammoniæ; considerable quantities are also used in the ammoniacal process for manufacturing soda ash.

Ammonium Chloride.

Ammonium chloride, muriate of ammonia, sal-ammoniac is the oldest known ammonium salt, and was prepared in quantity already by the Arabs. In Europe (Scotland) it has been manufactured since 1750. Its properties are described at p. 317. It can be prepared in various ways—either by direct saturation of gas-liquor or similar ammoniacal liquids (*e. g.* from the manufacture of bone-charcoal, or from putrefying urine), or by decomposing ammonium sulphate with sodium chloride, or by passing ammonia vapour into hydrochloric acid.

This last process is not much used. It has the drawback that no metal vessels, not even lead ones, resist the action of hot hydrochloric acid; and much acid and ammonium chloride is carried away by the hot vapours. Still this process is carried on at some places in France. More rational is the plan followed at a French works where the concentrated solution of ammonium carbonate and sulphate, obtained by one of the above-described apparatus (*e. g.* Mallet's or Grüneberg's), is mixed with hydrochloric acid in a vessel lined with lead and provided with a pipe for carrying away the vapours, in such manner that both liquids run in at the same time and that a nearly neutral but faintly acid liquid is formed. Whenever the vessel is full, the supply is stopped and the liquor is concentrated by a steam-coil up to the crystallizing-point. When a solution of ammonium chloride is boiled down in iron vessels, as is done (especially in England) in order to permit direct firing and saving fuel, the liquid must always be kept alkaline, and the loss of ammonia occurring during the evaporation by the dissociation of a little ammonium chloride must always be made up. If the liquid once becomes acid, it quickly dissolves iron and forms ferro-ammonium chloride, which is not decomposed by an excess of ammonia. Evaporating in lead is dearer, but much safer, if contamination with iron has to be avoided.

When ammonium chloride is to be made from sulphate, a concentrated solution of the latter is mixed with the equivalent quantity of common salt, and the whole is well agitated, and boiled down, during which process monohydrated sodium sulphate is precipitated and ammonium chloride remains in solution :



The sodium sulphate is fished out with perforated spades, and drained on copper plates, the liquor always running back into the pan. The salt is washed with a little water. The evaporation is continued till no more coarse crystals fall down and the liquid begins to be covered with an opalescent pellicle of salt, which shows that the sodium sulphate is nearly all removed. The liquid is now allowed to cool in leaden vessels; and the crystallizing ammonium chloride is first washed with a solution of the pure salt, then with pure water.

At some English works sal-ammoniac is still made by direct saturation of gas-liquor with hydrochloric acid, mechanically agitated. The escaping noxious gases are conveyed into the boiler-fire and burned. The faintly acid solution is left to settle; in three or four days the tar has separated out at the bottom of the vessel. Sometimes it is necessary to pass the liquid through canvas filters. The solution of ammonium chloride, still dark brown, is evaporated by direct fire in iron pans, and is always kept neutral or faintly alkaline by means of a little lime, chalk, or ammoniacal liquor. During the evaporation tarry oils are again separated, and are skimmed off along with a little ferric oxide. When the liquor has got up to 75° Tw., it is run into tubs 8 feet wide and 2½ feet deep, where its crystallization is finished in eight or ten days. Every six or eight hours it is stirred up in order to get small crystals, which are better for subliming. At last the mother liquor is run off by a plug-hole in the bottom, which is best made to slope to one side.

The crude ammonium chloride is coloured more or less dark by tarry matters, and contains other impurities, especially ammonium sulphate and thiosulphate, as well as moisture. It is dried in layers 4 inches thick, on metal plates heated by the waste heat of the subliming-pans, but not to the point of volatilization. Here the water and free acid are volatilized, and the tarry matters are mostly carbonized. The roasted salt is of a grey-white colour, and ought

to be conveyed as quickly as possible into the subliming-pots, lest it should again attract moisture.

Formerly the *subliming* was done in long rows of earthenware pots or glass carboys. But this was expensive, on account of the labour and the loss of the vessels in each operation. Hence, at least in England, iron pots are exclusively used, either cast in one piece or composed of several pieces, of 3 to 9 feet diameter. Large pots are far preferable to small ones, as these require hardly less fuel, labour, and time for working off than those. They are lined with fire-bricks, and are heated by a fire from below and by annular flues all round. Their bottom is, by preference, concave, so as to present a larger heating-surface. The pots are covered with concave plates, furnished in three places with rings for chains, by means of which they can be lifted off by a travelling crane &c. The covers are perforated in the centre; the aperture is closed by an iron rod, which is removed from time to time to allow the permanent gases to escape. They are covered with some non-conductor of heat. Pots 3 feet wide hold 10 cwt., those 5 feet wide 15 to 18 cwt.; those 9 feet wide, 2 to 2½ tons of salt.

The operation must be exactly regulated. At first a sharp fire is made; but this is slackened directly the sublimation commences, since at a very high temperature too much empyreumatic matter is evolved and disturbs the solidification of the salt. At too low a temperature the sublimate is loose and not transparent, which makes it difficult to sell. The cover ought to be at such a heat that a drop of water begins to boil on it and evaporates quickly. The first layer adhering to the cover is always brownish, probably because a little water always remains in the roasted salt which condenses on the cover and loosens ferric oxide. Later on a coloration may be caused by ferric oxide. The sublimation may last from 5 to 9 days, but is usually interrupted every week by lifting the cover, the fire having been damped up some time before. The sublimation is not driven to the last; for then the temperature would rise too high, the carbonaceous impurities would be decomposed and the vapours would injure the appearance of the sal-ammoniac. On the cover is found a layer from 2½ to 4 inches thick, which is knocked off. The above-mentioned brown stratum is knocked off with a hatchet or planed off.

In some treatises it is recommended to mix the salt before subliming with one third of its volume of animal charcoal, so as to obtain a purer sublimate; but this is too expensive for the manu-

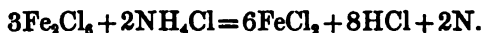
facturing-scale. On the contrary, some consumers, especially in France, require the sublimed sal-ammoniac to look as grey and dirty as that formerly made in Egypt from camels' dung; this is effected by adding some greasy matter to the salt before sublimation, so that some soot gets mixed with the sal-ammoniac. Otherwise this ought to be white, transparent, of fibrous texture, and firm, not porous and light.

Calvert proposed, in order to make the sublimation cheaper and continuous, and to obtain the product in a shape more convenient for use, to dry the muriate of ammonia very briskly and distil it from a set of fireclay retorts, alternately charged, into large brick chambers covered with a smooth coating of cement inside, on which the sal-ammoniac would be deposited as a fine powder. This process, which looks very rational indeed, was tried on the large scale, but was given up again and is not in use anywhere at present, probably just because the consumers insist upon the fibrous transparent texture of the product, which they believe (although erroneously) to guarantee its purity. Calvert also tried adding animal charcoal and phosphates before subliming; but his sal-ammoniac was never free from iron.

Besides sublimed sal-ammoniac, the crystallized salt, usually called *muriate of ammonia*, is also found in the trade, at a much lower price. To obtain this, the crude salt is once or more times recrystallized, and the solution each time filtered through animal charcoal. It is also made into the shape of loaves, the crystals being stirred up to a paste with a hot saturated solution, and the whole being allowed to solidify in conical sugar-moulds of glazed earthenware. The opening at the bottom is at first closed up by a plug, which is removed after a few days; the mother liquor then drains off. The loaves are taken out by inverting the moulds, and are dried in a stove; they turn nearly as hard as loaf sugar. Most ammonium chloride, however, is sold in the form of sublimed sal-ammoniac.

This salt is used chiefly in pharmacy, in soldering, in galvanizing iron, in dyeing and calico-printing, and in the manufacture of colours. For the latter purpose it should in general be free from iron. Formerly it was believed that this was always the case with colourless sal-ammoniac; but Wurtz has shown that only ferric chloride is indicated in sal-ammoniac by the ordinary reagents, while ferrous chloride cannot be discovered either by the colour or

by the ordinary reagents. The ferrous can be formed from the ferric chloride by the reducing action of sal-ammoniac itself, thus :—



In order to make a product entirely free from iron, a little chlorine gas is passed through the boiling-hot solution of ammonium chloride (an excess of chlorine would produce that fearfully explosive substance nitrogen chloride); ammonia is added, which precipitates all the iron now present as peroxide; the liquid is quickly filtered and crystallized. A salt free from iron is said to be obtained also by adding a little calcium phosphate before sublimation.

Ammonium Carbonate.

Commercial carbonate of ammonia (sal volatile), as has been explained on p. 815, is really a mixture or a compound of ammonium bicarbonate and carbamate, and as such is always formed on subliming. Hence the name frequently used for it, "ammonium sesquicarbonate," is incorrect, although the salt actually contains four molecules of NH_3 to three of CO_2 .

It is usually made by mixing ammonium sulphate with calcium carbonate and subliming. Calcium sulphate remains behind in the retort; and the mixture of ammonia, carbon dioxide, and aqueous vapour (which must not be absent) condenses on cooling to solid carbonate of ammonia. A mixture of 1 part ammonium sulphate with $1\frac{1}{2}$ or 2 parts of finely ground chalk, sometimes with a little charcoal powder, is heated in horizontal cylindrical cast-iron retorts, several of which are usually heated by the same fire, like gas-retorts. At first the heat should not be great; but at last it must attain redness.

The vapours are conveyed by a wide pipe into lead chambers, usually two or more in succession, provided with a door for the removal of the salt. From the last chamber the vapours pass through sulphuric acid, preferably trickling down in a small leaden coke-tower. In the chambers the condensation is effected solely by air-cooling; but they may be surrounded by a jacket to cool them by water. Several operations are performed in succession, till a sufficiently thick crust has formed, which is loosened by blows outside with a hammer, and is completely broken off after opening the doors. This crust must not be allowed to become too thick,

as otherwise the air-cooling will be too imperfect and the salt will become too hard and difficult to detach.

A convenient plan is, to employ five retorts, 18 inches in diameter, and 7 feet long, heated by one fire, with two condensing-chambers, each 8 or 10 feet long and wide and 7 feet high. The retorts may be charged alternately every eight hours. Each retort-cover has an aperture for a rake, to stir up the mass during the operations. The process in such an apparatus can go on for a fortnight before the chambers need be emptied, when the men adopt the precaution of tying sponges drenched in vinegar in front of their mouths and noses. During the work care must be taken lest the connecting pipes between the retorts and chambers get choked up.

In the bottom of the condensing-chambers is a pipe for running off a little solution of ammonium carbonate, formed from the excess of moisture; here also a little steam escapes.

The product of this first operation is still very impure, at least if crude ammonium sulphate has been employed; it is then discoloured by tarry matters and is sometimes sold as "ammonium carbonicum pyro-oleosum." It also mostly contains a little chalk or calcium sulphate carried over. Usually it is converted by resubliming into a white salt, forming fibrous transparent cakes 2 inches thick. This can be done at next to no expense, by the waste heat of the retort-furnace, which travels underneath a row of iron pots, covered with lead cylindrical caps. The crude salt is put into the pots, along with a little water (without which the pure salt would not be transparent). Sometimes the pans are not exposed to the direct fire, but are placed in a common water-bath, heated by the waste heat of the retort-fire. A temperature of 70° suffices for resubliming; and it is best not to exceed this, because the salt turns out finer and less is lost by volatilization. The lead caps into which the salt is to sublime are made by rolling a sheet of lead into the shape of a cylinder, covering this at the top with a piece of sheet-lead and pasting up the joints with paper. When the sublimation is finished, the lead is rolled up, and the cake of salt can be taken out at once.

Another apparatus for resubliming* consists of an iron pan 2 feet 6 inches wide at the bottom and 2 feet at the top, 15 feet long, and 2 feet 6 inches high, in the cover of which there are eight

* Bell, Chem. News, xii. p. 303.

12-inch holes, on which are placed conical lead caps, 2 feet 6 inches high, kept in their places by clamps or wedges. With these it is possible to work 14 days uninterruptedly. Then the clamps or wedges are loosened, and the mass is taken out; but it must be scraped off clean where it adheres to the lead. The salt is mostly packed in stone jars. In the iron pan remains some liquid, most of which is left behind for the next operation.

The usual process for making ammonium carbonate, as just described, is not quite rational. In the finished salt there is $1\frac{1}{2}$ times as much carbon dioxide as in the neutral salt; but according to the conditions of the process there is only enough CO_2 for the latter; hence a large quantity of ammonia must go away in the uncombined state. This might be remedied by passing carbon dioxide into the condensing-chambers; even an excess of this would not interfere with the formation of the ordinary ammonium carbonate (compare p. 315).

Even more direct is the process employed by Kunheim & Co. at Berlin, who bring together the gaseous mixture from the distillation of gas-liquor with carbon dioxide in lead chambers, and thus produce the commercial salt.

Pure ammonium carbonate (compare its properties, p. 315) is quite white, and at a fresh fracture shining and transparent, but is soon covered in the air with a fine dust of ammonium bicarbonate, ammonia being given off. On being heated it should volatilize completely and without empyreumatic smell; tarry matters are betrayed by a brown colour of the aqueous solution. The salt intended for analytical chemists should, after being neutralized with nitric acid, give no reaction with silver nitrate for chloride, or with barium salt for sulphate. Lime is indicated by a fixed residue and by ammonium oxalate; lead (which is to be avoided when the salt is to be employed as a baking-powder) by hydrogen sulphide. Sometimes thiosulphate is found by dissolving in acetic acid and adding silver nitrate, which produces a white precipitate, turning brown in a few moments.

This salt is principally employed for scouring wool, in dyeing, as a baking-powder, &c.

Ammonium Sulphocyanide.

This salt has lately come into somewhat extensive use, especially in dyeing and calico-printing, both directly and as a starting-point

for the preparation of other sulphocyanides* ; hence it is manufactured on an industrial scale. We pass over its preparation by a synthetical method †, and only mention its recovery from ammoniacal gas-liquor. It remains behind when the volatile ammonium compounds are expelled by steam. From this residue cupreous sulphocyanide can be obtained by adding a mixed solution of the sulphates of iron and copper. This was done by P. Spence ‡, who, after washing the precipitate, decomposed it by ammonium sulphide into copper sulphide and ammonium sulphocyanide. Similar to this, but hardly preferable, is the process of Storck & Strobel §, who saturate gas-liquor with hydrochloric acid and precipitate the sulphocyanide by a mixture of cupric chloride and sodium bisulphite. The precipitate is washed, boiled with a solution of barium hydrate, and the barium sulphocyanide allowed to crystallize. Phipson || mentions another process known in London, but does not say in what it consists.

ESTIMATION OF AMMONIA, FREE OR COMBINED.

We have already (p. 319) treated of the valuation of gas-liquor ; but we have yet to describe that of the sulphate and the other ammonium salts, and the preparation of the standard liquids.

The former processes for estimating ammonia, especially as ammonio-platinic chloride, are very seldom used now. For pure liquor ammoniæ the hydrometer is sufficient ; but it is not so when foreign salts are present, which make the percentage of ammonia appear too low. The only certain process is :—estimating the ammonia directly ; best of all, volumetrically. We have already seen (p. 320) that this can be done directly not merely with free ammonia, but also with ammonia combined with weak acids (CO_2 , H_2S). If combined with strong acids, it must first be set free by treatment with a fixed alkali ; and consequently this is the only suitable method for estimating the ammonium sulphate. For this

* Compare Storck & Strobel, Dingler's Journal, ccxxxv. p. 156 ; Glenck, *ibid.* ccxli. p. 399.

† Compare especially Tscherniak & Günzburg's German patent, No. 3199 ; Dingler's Journal, ccxxxii. p. 80. A new patent was taken out by them in 1881 ; and an exact description of their newest plant is found in the 'Bulletin de la Société industrielle de Mulhouse,' 1882, p. 77.

‡ Chem. News, xviii. p. 119.

§ Dingler's Journal, ccxxxv. p. 156.

|| Chem. News, xviii. p. 131.

purpose the apparatus, fig. 71 (p. 321), can be strongly recommended.

The following details of the process have been found most suitable at the large works of Kunheim & Co., near Berlin. The bulk-sample is well ground up, the whole of it passed through a sieve with about 8 meshes per linear inch, and a small sample taken from it. Of this about 15 grams are weighed, dissolved to 500 cubic centimetres, 50 c. c. of this introduced without filtering into a 300-c.c. flask, and distilled with about 15 c. c. caustic-soda solution of sp. gr. 1.25 for three hours; the evolved gas is absorbed

Fig. 85.

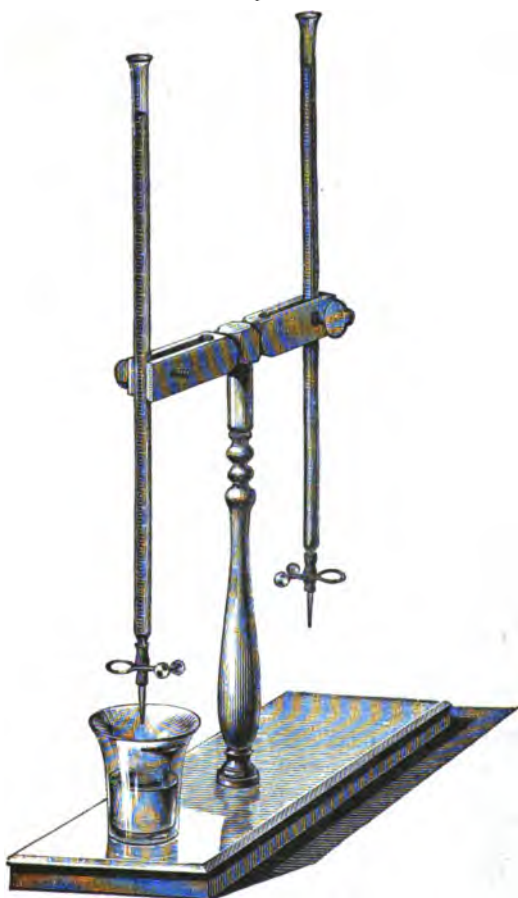


Fig. 86.



in 50 c. c. of seminormal standard acid, and titrated back with seminormal soda solution till purple.

As standard acid oxalic acid has been frequently recommended, but not justly. It is difficult to obtain it perfectly pure, and impossible to make sure that it contains neither too much nor too little water; hence the acid must always be tested in other ways. It is therefore best to employ at once, as cheaper and more stable, sulphuric or hydrochloric acid. The latter is preferable, since its strength can be exactly estimated in two different ways, viz. by titrating a known weight of freshly ignited pure sodium carbonate, and gravimetrically by means of silver nitrate. The standard acid is either made normal, so that 1 c. c. contains 0.049 gram SO_4H_2 , or 0.0365 HCl, and indicates 0.017 grm NH_3 , or $\frac{1}{4}$, $\frac{1}{5}$, or $\frac{1}{10}$ of that strength. The standard acid is kept in large bottles protected from great changes of temperature; whenever smaller stock bottles or the burettes are to be filled with it, the large bottle ought to be agitated in order to mix its contents with any moisture evaporated and again condensed in the empty upper part of the vessel. The burettes employed are always Mohr's (fig. 85), preferably with Erdmann's float (fig. 86). The standard alkali for retitrating the acid partly saturated by the evolved ammonia, is preferably not caustic potash or soda, but ammonia or caustic baryta. Normal ammonia would lose too much NH_3 on keeping; but seminormal ammonia (=0.0085 gram NH_3 per c. c.) keeps in well-stoppered bottles a very long time without change, and still more so quinti- or decinormal liquid. From time to time its strength should be controlled by standard acid. The advantage of ammonia is that it does not attract carbon dioxide, like caustic potash or soda, which makes the passage from one colour into the other much more distinct.

In agricultural laboratories especially, baryta-water is very much employed, which in the nature of things must be free from carbonic acid and hence gives very sharp final reactions. It cannot very well be made more than quintinormal; and care must be taken that it is not changed by attracting CO_2 from the air, which would precipitate baryta as carbonate. This is done, by means of the apparatus fig. 87 (p. 368) * in which the burette is filled by opening the lateral pinch-cock; the air required to replace the baryta-water running out of the stock bottle is deprived of CO_2 by soda-lime.

* From Lunge's 'Sulphuric acid & Alkali,' vol. i. p. 46.

Fig. 87.

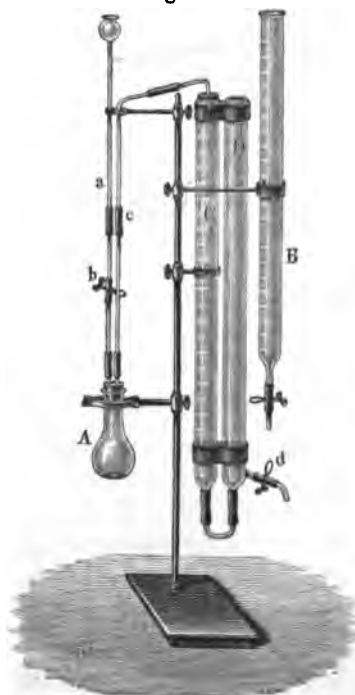


(N.B. The elastic tube at the top of the burette should not be connected with the soda-lime tubes, as is erroneously represented in the diagram.)

A better indicator than litmus is an alcoholic solution of corallin, whose purple-red colour is changed into light yellow by the slightest excess of acid, and *vice versa*. Of dimethylaniline-orange we have spoken at p. 320. If litmus is used with baryta-water, the end is attained when the red has changed into purple for the *first* time and remains so when the liquid is shaken. After a little time the red reappears again, which should not be taken into account.

Some agricultural chemists estimate the ammonia by combustion with soda-lime, in the way usual in organic analysis; but this is not at all to be recommended. Where many estimations have to be made, some prefer Knop's azotometer, fig. 88, which is founded on the fact that a solution of sodium hypochlorite containing bromine, or of sodium hypobromite, in the presence of a large excess of alkali, almost instantaneously liberates all the nitrogen of am-

Fig. 88.



monia salts. Such a solution is made by dissolving 200 grams of caustic soda in 1 litre of water, cooling the liquid (best by ice), and running in, with constant stirring, 25 grams of bromine. This solution does not keep very long, but decomposes, oxygen being given off. The nitrogen is liberated in the flask A, containing, up to a mark in its neck, 100 c. c.; it is measured in a gas-burette C, which likewise contains 100 c. c. and is divided into fifths of a cubic centimetre. The substance to be tested is dissolved in a 100-c.c. flask, the solution poured into the burette B, and 50 c.c. of it run into the flask A. Meanwhile the funnel tube *a* is filled with the hypobromite solution, and the pinch-cock *b* is opened, so that the liquid completely fills the lower part of the tube as well. By pouring water into D, after loosening the joint *c*, D and C are filled with water exactly to the mark for zero. Now the flask A is put to its cork, the joint at *c* is made again, and the apparatus is tried for tightness by running some water out of *d*; the level of the water in C will sink a little by the expansion of the air in A, but should become constant at once and remain so. Now by opening *b* a little hypobromite is run into A; the nitrogen is given off with effervescence and passes into C. From time to time a little water is run out of *d*, in order to prevent it from running over out of D. When the action slackens, more hypobromite is run in through the funnel till the liquid has reached the mark in the neck. Now all the nitrogen, and moreover 50 c. c. of air, have been forced over into C; to this must be added 0.3 c. c. for the air entering on attaching the india-rubber joint at *c*. The levels of the water in C and D are equalized, read off, and the volume of the nitrogen found by deducting 50.3 c. c. This volume must be reduced to 0° and 760 millimetres pressure by means of the formula

$$V_1 = \frac{Vb}{0.76 \times (1 + 0.003665 t)},$$

in which *b* is the height of the barometer reduced to 0° and diminished by the tension of aqueous vapour for the temperature *t*. All such reductions are facilitated by tables.

Each cubic centimetre of nitrogen at 0° and 760 millimetres pressure corresponds to 0.0012566 gram nitrogen or 0.0015259 gram ammonia. It should not be overlooked that only half of the substance weighed off has been employed for the testing, which with some practice is finished in a few minutes.

APPENDIX.

A. ADDENDA.

To p. 6. According to Roscoe*, the first product obtained in England from gas-tar was burning-naphtha, and only later on did Bethell's process for pickling timber point out a means of utilizing the heavy tar-oils. The total amount of tar distilled in one year (in Great Britain) now amounts to 410,000 tons.

Dr. Longstaffe † mentions that the first tar-distillery was erected by himself and Dr. Dalston near Leith in 1822, that the spirits went to Mr. Mackintosh for waterproofing, and the residue was consumed for the purpose of making lamp-black.

To p. 11. *The manufacture of a special quality of tar* in making illuminating-gas is touched upon in a German patent by Hegener (No. 14,889). He provides the gas-retorts with two separate hydraulic mains, the dipping-pipe to be opened or closed by means of a special valve. After charging and closing the retorts, the first, poor gas is sent through one main; at a latter stage, when it is richer in tar, containing much benzene, and of higher illuminating-power, it is sent through the other main, and towards the end, when it turns poorer again, once more through the first main.

To p. 43. *Xylene*. O. Jacobsen (Berl. Ber. 1881, p. 2628) has now found up to 25 per cent. orthoxylene in some crude xylene from coal-tar, which agrees with the author's supposition (p. 44).

To p. 48. *Dimethylnaphthalene*. Emmert and Reingruber (Liebig's Annalen, vol. cxi. p. 365), have recognized the fractions of

* Proceed. Soc. Chem. Ind. 1881, p. 8.

† Ibid. p. 13.

coal-tar boiling between 252° and 270° , after removing all acid, basic, oxygenated, and crystallizable components, as a mixture of several isomeric dimethylnaphthalenes, the separation of which has hitherto proved unmanageable. This research (along with that mentioned on p. 48) seems to prove that the *liquid* "indifferent" tar-oils which form a portion of creosote oil, essentially consist of methylated derivatives of naphthalene.

To p. 91. *An apparatus for separating tar and ammoniacal liquor* has been patented in Germany (No. 15,255), by the Berlin-Anhalt engine-works. Three vessels are placed, the second a little lower than the first, and the third a little below the second, the two former being heated by indirect steam. The mixture overflows from the upper into the next lower one, by a broad flat shoot. The bottom tank is the proper separator, where the tar flows underneath a partition and rises up at one side of the tank, whilst the ammoniacal liquor overflows at the other side, a partition holding back the tar-scum.

To p. 115. A further contribution to the *theory of fractional distillation* is contained in a paper by Konovalow, Ber. d. deutsch. chem. Ges. 1881, pp. 2224 & 2678.

To p. 177. *An investigation of the substances occurring in commercial crude anthracene* has been made by Zeidler (Ann. Chem. Pharm. cxi. p. 285). His results confirm those of former observers.

To p. 187. *Analysis of commercial anthracene**.—Paraffin (the objectionable presence of which in some samples of anthracene has been mentioned on p. 172), can be detected and determined in the following manner:—10 grams of the sample is heated with 200 grams of strong sulphuric acid in a water-bath for about ten minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c. c. of water contained in a tall beaker. After being thoroughly stirred, the liquid is allowed to cool, when any paraffin will rise to the surface and, having solidified, can be removed, washed with a little cold water, dried between blotting-paper, and weighed. From 2 to 5 per cent. is the quantity commonly present in Scotch anthracenes.

Mr. B. Nickels has communicated to Mr. Allen the following process for testing anthracene, employed at some alizarine-works,

* From the second volume of Allen's 'Commercial Organic Analysis,' which appeared too late to be used in the text.

of which the aim is to work as closely as possible by the method of oxidation pursued on a manufacturing-scale.

With this view, the oxidation is carried out in very dilute liquids, under which conditions the anthracene is converted into anthraquinone, while the foreign hydrocarbons suffer but little change. On subsequently treating the product with sulphuric acid, the unoxidized hydrocarbons are converted into soluble substances, and a nearly pure anthraquinone results, which may be obtained perfectly pure by a second treatment with acid. In experienced hands and with careful manipulation, this miniature factory-operation gives constant and very accurate results.

The chief source of error is incomplete conversion of the anthracene itself, and its consequent solution and loss on treating the crude anthraquinone with sulphuric acid; but this can be guarded against by a microscopic examination of the oxidation-product. The following are the details of the process:—Ten grams of the sample of anthracene are ground to an impalpable powder in a mortar; 20 grams of potassium bichromate are added, and the whole thoroughly mixed by grinding; the mixture is transferred to a large porcelain dish, 1 litre of water added, and the liquid brought to boil; 30 grams of sulphuric acid are diluted with about an equal measure of water, and added in successive small portions during about one hour, the liquid being kept constantly boiling and frequently stirred. The boiling is continued for three hours after the whole of the acid has been added, care being taken to replace the loss by evaporation by adding boiling water, as it is only in such dilute solution that the anthracene can be converted into anthraquinone, without simultaneously oxidizing the accompanying substances. The liquid is next filtered, and the filter washed with hot water till all traces of chromium salts have been removed. The contents of the filter are then dried at 100° and weighed. The weight obtained represents the yield of "crude factory anthraquinone," and may contain from 40 to 50 per cent. of the pure substance. Before purifying this crude product a minute quantity of it should be dissolved in hot benzene, and a drop of the solution placed on a glass slide. After allowing the dissolved matters to crystallize, a glass cover is applied, and the slide observed under the microscope. Unoxidized anthracene, if present, assumes the form of sharp, tabular, overlapping plates; while the anthraquinone will be in the form of distinct needles and stellate

groups. Naphthalene is the only associated hydrocarbon which at all simulates anthracene; but with a little care it is readily distinguished. The other bodies liable to be present assume more or less characteristic forms, which cannot be confounded with anthracene. Examined with the polariscope, the appearances of anthracene and anthraquinone are extremely characteristic. If no unoxidized anthracene be detected under the microscope, the purification of the crude anthraquinone is proceeded with as follows:—

The crude anthraquinone is next treated in a small shallow dish with four times its weight of strong sulphuric acid; and the mixture is heated in the water-oven for about one hour and a half, being frequently stirred during that time. The capsule is then placed in a box, or under a bell-jar, side by side with a larger dish of boiling water, so as to maintain a damp atmosphere, which causes the gradual dilution of the acid and facilitates the crystallization of the anthraquinone. After twelve hours the capsule is removed and immersed in about 500 c. c. of water, which is then boiled. After cooling, the liquid is filtered, the residue washed till free from acid, and then treated on the filter with a dilute boiling solution of caustic soda (sp. gr. 1.04), till the filtrate runs through colourless. The alkali is then washed out with warm water, and the substance on the filter dried at 100° C. and weighed. The product has a greenish grey or slate-grey colour, is highly crystalline and contains from 80 to 95 per cent. of real anthraquinone. A known weight of it (about 1 gram) is further purified by heating it in the water-oven for ten minutes with ten times its weight of strong sulphuric acid. The product is exposed to a damp atmosphere, dissolved in water, filtered, treated with alkali, &c., and weighed in a manner exactly similar to that previously adopted. The usual precautions respecting the treatment of the anthraquinone on the filter should be observed here. The weight of pure anthraquinone obtained is calculated first on the grey product, and this on the original sample, or immediately on the crude anthraquinone, if some of the latter was not recovered from the benzene solution used for its microscopic examination. The pure anthraquinone found, multiplied by .856, gives the real anthracene in the sample.

B. TABLES.

TABLES I., II., III.

(for reducing the specific gravities of liquids lighter than water to the normal temperature of $15^{\circ}5$ C., = 60° F.).

Note. The scale of reduction is not the same for high and low temperatures; hence three tables are given. When the observed temperature is *below* the normal, the figures in the table must be *deducted* from the observed specific gravity in order to reduce this to the normal temperature, and *vice versa*.

I. For Specific Gravities from 0.880 downwards.

Degrees C.	2	4	6	8	10	12	13½	15½
Deduct ...	0.0105	0.009	0.008	0.006	0.0045	0.003	0.002	0
Degrees C.	17½	19½	21½	23	25	27	29	
Add	0.001	0.0025	0.004	0.0055	0.007	0.008	0.010	

II. For Specific Gravities between 0.880 and 0.920.

Degrees C.	2	4	5½	7	9	10½	12	14
Deduct ...	0.010	0.0085	0.0075	0.0065	0.005	0.004	0.0025	0.001
Degrees C. .	15½	17	19	20½	22	24	25½	27
Add	0	0.001	0.0025	0.0035	0.005	0.006	0.007	0.0085

III. For Specific Gravities between 0.920 and 0.960.

Degrees C.	1½	3	4½	6	7	8½	10	11½	13	14	15½
Deduct ...	0.010	0.009	0.008	0.007	0.006	0.005	0.004	0.003	0.002	0.001	0
Degrees C.	17	18	19½	21	22½	24	25	26½	28	29½	
Add	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009	0.010	

TABLE IV.

(for comparing the degrees of Baumé, Cartier, and Beck with the corresponding specific gravities, for liquids lighter than water).

Degrees.	Baumé.	Cartier.	Beck.	Degrees.	Baumé.	Cartier.	Beck.
0	1.0000	17	0.952	0.955	0.9090
1	0.9941	18	0.946	0.948	0.9042
2	0.9883	19	0.940	0.941	0.8994
3	0.9826	20	0.933	0.934	0.8948
4	0.9770	21	0.927	0.928	0.8900
5	0.9714	22	0.921	0.921	0.8854
6	0.9659	23	0.915	0.914	0.8808
7	0.9604	24	0.909	0.908	0.8762
8	0.9550	25	0.903	0.901	0.8717
9	0.9497	26	0.898	0.895	0.8673
10	1.000	...	0.9444	27	0.892	0.889	0.8629
11	0.993	1.000	0.9392	28	0.886	0.883	0.8585
12	0.986	0.992	0.9340	29	0.881	0.877	0.8542
13	0.979	0.985	0.9289	30	0.875	0.871	0.8500
14	0.972	0.977	0.9239	31	0.870	0.865	0.8457
15	0.966	0.970	0.9189	32	0.864	0.859	0.8415
16	0.959	0.962	0.9139				

TABLE V.

(for comparing the Centigrade and Fahrenheit's Thermometer).

C.	F.	C.	F.	C.	F.	C.	F.
+500	+932	+74	+165.2	+45	+113	+16	+60.8
400	752	73	163.4	44	111.2	15	59.0
300	572	72	161.6	43	109.4	14	57.2
200	392	71	159.8	42	107.6	13	55.4
100	212	70	158	41	105.8	12	53.6
99	210.2	69	156.2	40	104	11	51.8
98	208.4	68	154.4	39	102.2	10	50.0
97	206.6	67	152.6	38	100.4	9	48.2
96	204.8	66	150.8	37	98.6	8	46.4
95	203	65	149	36	96.8	7	44.6
94	201.2	64	147.2	35	95	6	42.8
93	199.4	63	145.4	34	93.2	5	41.0
92	197.6	62	143.6	33	91.4	4	39.2
91	195.8	61	141.8	32	89.6	3	37.4
90	194	60	140	31	87.8	2	35.6
89	192.2	59	138.2	30	86	1	33.8
88	190.4	58	136.4	29	84.2	0	32.0
87	188.6	57	134.6	28	82.4	- 1	30.2
86	186.8	56	132.8	27	80.6	2	28.4
85	185	55	131	26	78.8	3	26.6
84	183.2	54	129.2	25	77.0	4	24.8
83	181.4	53	127.4	24	75.2	5	23.0
82	179.6	52	125.6	23	73.4	6	21.2
81	177.8	51	123.8	22	71.6	7	19.4
80	176	50	122	21	69.8	8	17.6
79	174.2	49	120.2	20	68.0	9	15.8
78	172.4	48	118.4	19	66.2	10	14.0
77	170.6	47	116.6	18	64.4	11	12.2
76	168.8	46	114.8	17	62.6	12	10.4
75	167						

All the temperatures mentioned in this book are in Centigrade degrees, but can be converted into Fahrenheit degrees by means of the above Table.

ERRATA.

Page 4, line 2 from the bottom, <i>read</i> coking				<i>instead of</i> cooling.	
" 12, "	" 15	" the top	" and the anthracene	"	the anthracene.
" 22, "	" 3	" "	" paraffins	"	paraffin.
" 22, "	" 12	" "	" process	"	process.
" 36, "	" 10	" "	" glass tube	"	tube.
" 40, footnote			" Thomsen	"	Thomson.
" 46, line 5 from the top			" ethylene	"	acetylene.
" 46, "	" 16	" "	" sulphonic acid	"	sulpho-acid.
" 46, "	" 19	" "	" nitric	"	sulphuric.
" 68 "	" 19	" "	" $\text{CH}_3 \cdot \text{SH}$	"	$\text{CH}_3 \cdot \text{S}$.
" 139, "	" 16	" "	" $19\frac{1}{4}$ tons.	"	$19\frac{1}{4}$ cwt.

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THE END.

